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DETERMINATION OF SMALL AMOUNTS OF COBALT IN TITANIUM, ZIRCONIUM AND THEIR ALLOYS

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Summary—To fulfil the need for a method of determining cobalt, over the range 50 to about 2 ppm, in titanium, zirconium and their alloys, a direct absorptiometric procedure has been developed. This procedure is based on the formation of an orange-coloured cobalt/nitroso-R-salt complex, in a solution of controlled acidity (about pH 6). Hydrolysis of salts at this pH is prevented by the addition of ammonium fluoride.

Tests have shown that, in the presence of titanium, up to at least 20% of manganese, 10% of aluminium or 5% of iron are without effect and, in the presence of zirconium, up to at least 5% of lead, aluminium, iron, manganese, zinc, magnesium or tungsten do not interfere.

Simple modifications to the procedure overcome interference by tin or molybdenum up to 20%, copper, chromium or vanadium up to 5%, or nickel up to 2·5%.

The procedure is simple, rapid and particularly suitable for the examination of reactor-grade zirconium, where the limit of cobalt is usually less than 20 ppm. The standard deviation at the 20-ppm level is about 0·3 ppm.

INTRODUCTION

Cobalt may be introduced into titanium, zirconium and their alloys from the parent ores. The amount of contamination is of metallurgical interest, especially in zirconium-bearing materials used in nuclear reactors, where only small amounts of cobalt, not more than about 20 ppm, can be tolerated because of its high neutron-capture cross-section. Titanium has been suggested as a suitable material for certain ancillary equipment in nuclear reactors and the presence of more than a few parts per million of cobalt in such material could be a serious disadvantage because of the formation of cobalt 60, a strong γ-emitting isotope with a half-life of 5·25 years. These factors have necessitated provision of a reliable procedure for determining cobalt over the range 50 to about 2 ppm in titanium and zirconium bearing materials.

Absorptiometric methods based on the use of β-nitroso α-naphthol, *o*-nitroso-cresol, ammonium thiocyanate[1,2,3] and nitroso-R-salt[4–7] have been recommended for determining small amounts of cobalt in a variety of materials including soils, animal organs and metallurgical products. Consideration of these and other methods published in the literature indicated that a procedure based on formation of an orange-coloured cobalt/nitroso-R-salt complex should be most suitable for determining small amounts of cobalt in the materials under examination. The cobalt complex is formed in a solution with a pH of about 6, controlled by means of a buffer of either sodium acetate[4] or citrate/phosphate/borate;[5] mineral acid (usually nitric acid) is subsequently added to decompose complexes of interfering metals. Maximum absorption of the complex occurs at about 4200 Å but at this wavelength nitroso-R-salt solution also absorbs strongly. The procedure adopted, therefore, is either to destroy excess reagent by bromination[5] or to measure the absorption at 5500 Å, a wavelength at which absorption due to the reagent solution is negligible.

Because orthophosphates of titanium and zirconium are only slightly soluble, a procedure using a sodium acetate buffer[4] was chosen as a basis for investigation. To obtain maximum sensitivity it was proposed to destroy excess nitroso-R-salt and measure the optical density of the solution at the wavelength of maximum absorption of the complex.

EXPERIMENTAL

Cobalt in titanium

Initial tests in the presence of titanium showed that the sample (0·25 g) must be dissolved in a minimum amount of acid in order to obtain suitable conditions for subsequent adjustment of the pH of the solution to about 6. To prevent hydrolysis of titanium salts at this pH, it was necessary to add a complexing agent before adding the buffer solution. Using either sodium citrate or sodium tartrate to form a complex with titanium, full colour development of the cobalt/nitroso-R-salt was not obtained and results were erratic. Consistent results were obtained, however, when ammonium fluoride was used as a complexing agent. A buffer solution of ammonium acetate was added in place of sodium acetate in order to avoid precipitation of sodium fluorotitanate, which is less soluble than the corresponding ammonium salt. With these, and other minor modifications to a provisional procedure, tests were made in the presence of titanium to establish the wavelength at which maximum absorption of the cobalt/organo complex occurs and, using this wavelength, to prepare a calibration graph.

Absorption curve: High purity cobalt (0·5 g) was dissolved in 25 ml of sulphuric acid (1 + 4), the solution was transferred to a 1-litre calibrated flask and diluted with water, to the mark. A 10-ml aliquot of this solution was diluted to 500 ml in a calibrated flask; then:

$$1 \text{ ml} \equiv 0{\cdot}01 \text{ mg of cobalt.}$$

"Iodide" titanium (high-purity prepared by the van Arkel process) (0·25 g) was dissolved by gently heating in a mixture of 10 ml of sulphuric acid (1 + 49) and 1 ml of fluoroboric acid; 1·0 ml of the standard cobalt solution (1 ml ≡ 0·01 mg of cobalt) was added and the solution was oxidised with a minimum of concentrated nitric acid, added dropwise. Ten ml of ammonium fluoride solution (10%) were added, the solution was heated to boiling and, whilst still hot, additions were made of 0·5 ml of nitroso-R-salt solution (0·2%) and of 10 ml of ammonium acetate solution (50%). The solution was set aside for 5 minutes, 5 ml of concentrated nitric acid were added and, after 5 minutes, 0·5 ml of saturated bromine water. After a further 5 minutes bromine was removed by boiling the solution for about 5 minutes. The cooled solution was filtered into a 50-ml calibrated flask and diluted to the mark. Optical density measurements were made at 20°, using a Unicam S.P.600 Spectrophotometer (4-cm cells) at wavelengths ranging between 3600 Å and 5200 Å. The maximum absorption was at 4200 Å.

Calibration graph: Solutions were prepared, as in the foregoing paragraph, containing 0·25 g of iodide titanium and standard cobalt solution (1 ml ≡ 0·01 mg of cobalt) in amounts ranging from 0 to 1·5 ml. Reagents were added as before, solutions were filtered into 50-ml calibrated flasks and diluted to the mark. Optical densities were determined at a wavelength of 4200 Å (4-cm cells) and a linear calibration graph was obtained, suitable for determining cobalt in the range 2 to 60 ppm.

Effects of temperature, reagent concentration and other factors: Tests showed that no significant variation in optical density of the complex occurred over the temperature range 18 to 25°, and strict control of solution temperature during optical density measurements was, therefore, not essential. The complex was stable for about 1 hour, after which the optical density slowly decreased.

Varying the amount of sulphuric acid between 7·5 and 12·5 ml had no significant effect. Below 7·5 ml of the acid, dissolution of the sample was difficult and above 12·5 ml optical density of the complex decreased. Varying the amount of fluoroboric acid between 0·5 and 2 ml had a negligible effect on the optical density, but below about 0·5 ml, titanium dissolved only with difficulty and the tendency for titanium salts to hydrolyse was increased.

Over the range 7·5 to 11 ml, the amount of ammonium fluoride solution (10%) had no significant effect on the optical density, but above this upper limit, optical density decreased with increase in amount of ammonium fluoride. Below 7·5 ml, precipitation of titanium hydroxide occurred when the solution was boiled.

Addition of nitroso-R-salt solution (0·2%) over the range 0·25 to 1·0 ml had a negligible effect, but the presence of more than 1 ml of the reagent caused a sharp increase in optical density which was attributed to incomplete decomposition of the reagent by 0·5 ml of saturated bromine water. Further tests showed that 1 ml of saturated bromine water was sufficient to decompose up to 5 ml of the reagent, and amounts up to 10 ml were completely decomposed by 2·5 ml of bromine water, without affecting the optical density of the cobalt/organo complex.

No effect on the optical density was observed when the amount of ammonium acetate buffer solution (50%) was varied between 5 and 10 ml. Using 2·5 ml of this solution, a slight decrease in optical density occurred; with amounts above 10 ml, results were both low and erratic. In subsequent tests, therefore, addition of 7·5 ml of ammonium acetate (50%) was made.

Over the range 4 to 10 ml, the amount of concentrated nitric acid (sp. gr. 1·42) had no significant effect. Below 4 ml, the optical density decreased sharply with decrease in nitric acid concentration; above 10 ml a slight decrease in optical density occurred. In subsequent tests, therefore, addition of 6 ml of concentrated nitric acid was made.

Tests to determine the effect of common alloying constituents and likely impurities (Table I) established that no interference was caused by the presence of at least 20% of manganese or 10% of aluminium.

Iron was not completely oxidised with nitric acid when followed by immediate addition of ammonium fluoride, even when ferrous sulphate equivalent to only 0·05% of iron was added to the 0·25-g sample of titanium. Iron remaining in the reduced state completely inhibited formation of the cobalt/organo complex. Further tests established that complete oxidation of iron was obtained by heating the solution at about 70° for 5 minutes, after addition of the nitric acid; in this way satisfactory results were obtained in the presence of at least 5% iron.

Tin formed a yellow-coloured compound with nitroso-R-salt and this complex had considerable absorption at 4200 Å. If present above about 0·1%, tin caused results to be erratic. Experiments showed that interference by tin, up to at least 20%, could be overcome by modifying the procedure so that tin was volatilised as stannic bromide; details are given in the Method. Chromium above about 0·25% interfered because of absorption at 4200 Å by green-coloured chromic ions, but interference by up to 5% of chromium could be overcome by measuring the optical density of the test solution against a similar solution prepared in the absence of the nitroso-R-salt. Nickel consumes the reagent and introduced error when present above about 0·1%, but provided the volume of nitroso-R-salt solution was increased by 0·5 ml for each 0·1% of nickel present, this error could be avoided; samples containing up to 2·5% of nickel have been satisfactorily examined in this way. Vanadium above about 0·25% interfered in the same way as nickel, but interference by as much as 5% of vanadium could be overcome by adding 1 ml of the reagent solution for each 0·5% of vanadium present; complexes of nickel and vanadium are destroyed when nitric acid is added. When vanadium is present, the optical density of the test solution is measured against a similar solution, prepared without the addition of nitroso-R-salt solution; this procedure compensates for absorption by greenish-blue coloured vanadium ions. Molybdenum, above about 0·005% caused high results due to absorption by green-coloured tervalent molybdenum ions, which were formed during solution of the sample and not oxidised by nitric acid. Provided molybdenum was oxidised to the sexavalent state (colourless), with potassium permanganate immediately after oxidation of titanium with nitric acid, and excess potassium permanganate was then reduced with sodium nitrite, up to at least 20% of molybdenum could be tolerated. Copper above about 0·025% caused results to be both low and erratic, but copper was precipitated during solution of the sample and the effect of up to about 5% of the metal could be rendered negligible, if the test solution was filtered through a No. 41 Whatman filter paper immediately after the sample had dissolved. Results of all tests on these metals are summarised in Table I.

Cobalt in zirconium

A calibration graph covering the range 2 to 60 ppm of cobalt, prepared in the presence of "iodide" zirconium, was identical with that obtained in the presence of titanium.

Effects of temperature, acidity, concentration of reagents and stability of the complex were studied in the presence of zirconium, in place of titanium, and results agreed with those obtained in similar experiments relating to the determination of cobalt in titanium.

Effects of common alloying constituents and likely impurities were also investigated in the presence of major amounts of zirconium, and Table II shows that up to at least 5% of lead, aluminium, iron,

Table 1.—Effects of other metals on the determination of cobalt in titanium
(0·25 g of titanium present in all tests)

Metal added %	Cobalt (*ppm*)		Remarks
	Added	Determined	
Manganese			
0·20	5	5	
0·20	50	50	
20·0	5	5	
20·0	50	49	
Iron			
0·05	5	5	Iron present as Fe^{III}
0·05	50	50	
5·0	5	5	
5·0	50	50	
Chromium			
0·05	5	5	
0·05	50	50	
0·25	5	5·5	
0·25	50	51	
0·50	5	6	
0·50	50	55	
0·50	5	5	Compensating solution containing chromium used as blank.
0·50	50	50	
5·0	5	5	
5·0	50	51	
Aluminium			
0·10	5	4·5	
0·10	50	50	
10·0	5	5	
10·0	50	49	
Tin			
0·05	5	5	
0·05	50	50	
0·10	5	5	
0·10	50	49	
0·25	5	4·5	
0·25	50	47	
1·0	5	5·5	
1·0	50	56	
2·0	5	5	Tin removed by bromination
2·0	50	50	
20·0	5	5	
20·0	50	50	
Vanadium			
0·10	5	5	
0·10	50	50	
0·25	5	5	
0·25	50	50	

Nickel			
0·025	5	5·5	
0·025	50	50	
0·10	5	5	
0·10	50	51	
0·25	5	4·5	
0·25	50	42	
0·25	5	5	Additional reagent added to test solutions.
0·25	50	49	
1·0	5	5·5	
1·0	50	50	
2·5	5	5·5	
2·5	50	50·5	
Copper			
0·01	5	5·5	
0·01	50	49·5	
0·025	5	5	
0·025	50	50	
0·05	5	4·5	
0·05	50	43	
0·10	5	4	
0·10	50	36	
0·05	5	4·5	Copper removed by filtration
0·05	50	47·5	
0·25	5	5	
0·25	50	49	
2·5	5	4·5	
2·5	50	48·5	
5·0	5	4·5	
5·0	50	49	
1·0	5	4·5	
1·0	50	25	
2·5	5	—	Cobalt complex not formed. Additional reagent added to test soln. and a compensating soln. containing vanadium used as blank.
2·5	50	—	
2·5	5	5	
2·5	50	50·5	
5·0	5	5	
5·0	50	51	
Molybdenum			
0·001	5	5	
0·001	50	50	
0·005	5	5·5	
0·005	50	50	
0·01	5	7·5	
0·01	50	60	
0·01	5	5	Molybdenum oxidised with potassium permanganate
0·01	50	50	
0·25	5	5	
0·25	50	50	
20·0	5	5	
20·0	50	49·5	

In all the above tests an equivalent weight of titanium was present in the compensating solution, thus correcting for the small amount of cobalt present in the parent material.

Table II.—Effects of other metals on the determination of cobalt in zirconium
(0·25 g of zirconium present in all tests)

Metal added %	Cobalt (*ppm*)		Remarks	Metal added %	Cobalt (*ppm*)		Remarks
	Added	Determined			Added	Determined	
Lead				Aluminium			
0·05	5	5		0·05	5	5	
0·05	50	49·5		0·05	50	51	
5·0	5	5		5·0	5	4·5	
5·0	50	50		5·0	50	50	
Iron				Manganese			
0·05	5	5		0·05	5	5	
0·05	50	50		0·05	50	50·5	
5·0	5	5·5		5·0	5	5	
5·0	50	49·5		5·0	50	50	
Zinc				Magnesium			
0·05	5	5		0·05	5	5·5	
0·05	50	50		0·05	50	50	
5·0	5	5		5·0	5	5	
5·0	50	50		5·0	50	50	
Tungsten				Tin			
0·05	5	5		0·01	5	5	
0·05	50	49·5		0·01	50	50	

5·0	5	5	
5·0	50	50	
Chromium			
0·05	5	5	
0·05	50	50	
0·25	5	5·5	
0·25	50	51	
5·0	5	5	Compensating solution containing Cr used as blank.
5·0	50	50	
Vanadium			
0·1	5	5	
0·1	50	50	
0·25	5	5	
0·25	50	49·5	
5·0	5	5	Additional reagent added to test soln. and a compensating soln. containing vanadium used as blank.
5·0	50	49·5	
Copper			
0·01	5	5	
0·01	50	50	
0·025	5	5	
0·025	50	49·5	
0·05	5	3·5	
0·05	50	36	
0·05	5	5	0·1 g Ti added and copper removed by filtration
0·05	50	48·5	
0·25	5	4·5	
0·25	50	47·5	
5·0	5	5	
5·0	50	47·5	
2·0	5	5	Tin removed by bromination
2·0	50	49·5	
20·0	5	5	
20·0	50	49·5	
Nickel			
0·025	5	5	
0·025	50	49	
2·5	5	5·5	Additional reagent added to test solns.
2·5	50	49·5	
Molybdenum			
0·5	5	5	
0·5	50	50	
2·5	5	5	
2·5	50	50	
5·0	5	5	
5·0	50	50	
10·0	5	7	
10·0	50	53	
10·0	5	5	Molybdenum oxidised with potassium permanganate
10·0	50	50	
20·0	5	4·5	
20·0	50	49	

In all the above tests an equivalent weight of zirconium was present in the compensating solution, thus correcting for the small amount of cobalt present in the parent material.

manganese, zinc, magnesium, or tungsten did not interfere. Interferences by tin, chromium, nickel and vanadium were similar to those obtained in the presence of titanium and the effects could be overcome by modifications described earlier. Molybdenum, above about 5%, caused high results, but interference by as much as 20% of the metal could be overcome by oxidising the solution with potassium permanganate as previously described.

Copper, above about 0·025%, caused results to be both low and erratic due to incomplete precipitation of copper during solution of the sample, but by adding titanium (0·1 g) to the weighed sample, precipitation of copper was rendered more complete. With this modification the method could be satisfactorily applied to samples containing up to at least 5% of copper, provided copper was removed by filtration.

APPLICATION OF THE METHOD

Procedures described in the Method were applied to samples of titanium, zirconium and several of their alloys, with and without the addition of 5 ppm of cobalt (added as cobaltous sulphate) and satisfactory results were obtained (Table III). Experience indicates that about 25 determinations can be made in 8 hours by one analyst. The standard deviation at the 20-ppm level is about 0·3 ppm.

METHOD

Reagents

Sulphuric acid (1 + 49): To about 100 ml of water add 5 ml of concentrated sulphuric acid (sp. gr 1·84) and dilute to 250 ml.

Table III.—Determination of cobalt in titanium, zirconium and their alloys

Sample No.	Nominal Composition	Cobalt (*ppm*)	
		Added	Determined
1	Commercially pure titanium	Nil 5 20	3 8 22·5, 23, 23 23, 22·5, 22·5
2	Titanium + 4% Al + 4% Mn (314A alloy)	Nil 5	<2 6
3	Titanium + 5% Al + 2·5% Sn (317 alloy)	Nil 5	2·5 7·5
4	Titanium + 2·5% Al + 13% Sn (371 alloy)	Nil 5	3 7·5
5	Titanium + 6% Al + 4% V (318A alloy)	Nil 5	<2 6
6	Commercially pure zirconium	Nil 5	<2 5·5
7	Zirconium + 1·5% Sn + 0·12% Fe + 0·1% Cr + 0·05% Ni (Zircaloy 2)	Nil 5	<2 6·5

Standard Deviation on Sample No. 1, at the 20 ppm-level is about 0·3 ppm.

Fluoroboric acid: To 280 ml of hydrofluoric acid (maintained at 10°) add, in small quantities, 130 g of boric acid. Store in a polythene bottle.

Ammonium fluoride solution: 10% : Dissolve 25 g of ammonium fluoride in about 150 ml of water, filter if necessary and dilute to 250 ml.

Nitroso-R-salt solution: 0·2%: Dissolve 0·2 g of nitroso-R-salt in about 75 ml of water and dilute to 100 ml.

Ammonium acetate buffer solution: 50%: Dissolve 125 g of ammonium acetate in about 150 ml of water and dilute to 250 ml.

Standard cobalt solution: Dissolve 0·5 g of high-purity cobalt in about 25 ml of sulphuric acid (1 + 4) and dilute to 1 litre.

Dilute 10 ml of this solution to 500 ml. Then:

1 ml ≡ 0·01 mg of cobalt.

Additional reagents for samples containing molybdenum

Potassium permanganate solution: 2%: Dissolve 2 g of potassium permanganate in about 75 ml of water and dilute to 100 ml.

Sodium nitrite solution: 0·1%: Dissolve 0·1 g of sodium nitrite in about 75 ml of water and dilute to 100 ml.

Preparation of Calibration Graph

Add, separately, 0·25, 0·5, 1·0 and 1·5 ml of the standard cobalt solution (1 ml ≡ 0·01 mg of cobalt) to each of four beakers. Add to each solution (and a blank) 10 ml of sulphuric acid (1 + 49) and a few drops of concentrated nitric acid (sp.gr. 1·42), then proceed with each solution as follows:

Add 10 ml of ammonium fluoride solution (10%), heat to boiling, allow to cool slightly and add 0·5 ml of nitroso-R-salt solution (0·2%) and 7·5 ml of ammonium acetate buffer solution (50%). Allow to stand for about 5 minutes, then add 6 ml of concentrated nitric acid and, after a further 5 minutes, add 0·5 ml of bromine water (saturated). Again allow the solution to stand for about 5 minutes, then boil for about 5 minutes to remove excess bromine, cool and filter through a No. 40 Whatman paper into a 50-ml calibrated flask. Dilute to the mark and measure the optical density at a wavelength of 4200 Å, using 4-cm cells, and preferably at 20°.

Procedure

(A reagent blank must be carried through the entire procedure.)

(*a*) *For samples containing less than* 0·1% *of tin:* Dissolve 0·25 g of the sample (Note 1) in 10 ml of sulphuric acid (1 + 49) and 1 ml of fluoroboric acid; warm gently, at about 70°, to assist solution. Add a few drops of concentrated nitric acid (sufficient to oxidise any titanous salts present) and allow to stand for 5 minutes to ensure complete oxidation of any iron present (Note 2). Add 10 ml of ammonium fluoride solution (10%), heat to boiling and continue as described for preparation of the calibration graph (Notes 3 and 4).

Calculate the cobalt content of the sample using the calibration graph.

(*b*) *For samples containing more than* 0·1% *of tin:* Dissolve 0·25 g of the sample in a mixture of 10 ml of concentrated hydrochloric acid (sp. gr. 1·18), 10 ml of hydrobromic acid (sp. gr. 1·5) and 0·25 ml of fluoroboric acid; warm gently to assist solution. Add 1 ml of bromine, evaporate the solution to dryness and bake at about 300° for 15 minutes. Cool, add a further 10 ml of hydrobromic acid and 1 ml of bromine; in adding these reagents, wash down the sides of the beaker. Evaporate to dryness, bake for a further 15 minutes, then fuse the residue in the beaker in 2 to 3 g of anhydrous sodium bisulphate. Cool, dissolve the fused residue in 10 ml of ammonium fluoride solution (10%). The precipitate of sodium fluoride which forms at this stage does not interfere. Heat to boiling and continue as described for preparation of the calibration graph.

Calculate the cobalt content of the sample using the calibration graph.

Notes

(1) Copper, above about 0·025%, interferes. This interference, up to about 5%, can be rendered negligible by filtering the solution (before nitric acid is added) to remove precipitated copper. In the examination of zirconium-bearing samples, it is necessary to add 0·1 g of titanium in order to ensure satisfactory precipitation of copper.

Interference by chromium, up to 5%, can be overcome by measuring the optical density of the test solution against a compensating solution, prepared by treating a separate sample as described in the procedure but in the absence of the nitroso-R-salt solution. The effect of chromium below about 0·25% is negligible.

(2) Molybdenum, above about 0·005%, interferes in the examination of titanium-bearing materials, and above about 5% in the examination of zirconium and its alloys.

Interference by molybdenum, up to 20%, can be overcome by oxidising the solution (after nitric acid oxidation) with potassium permanganate solution, added dropwise. Excess permanganate is then reduced by sodium nitrite solution, also added dropwise.

(3) Nickel, above about 0·1%, interferes, but the effect of this metal, up to about 2·5%, can be overcome by adding 0·5 ml of nitroso-R-salt solution for each 0·1% of nickel present.

When vanadium is present over 0·25%, up to about 5%, add 1 ml of nitroso-R-salt solution for each 0·5% of vanadium present, and measure the optical density of the test solution against a compensating solution, prepared in the absence of the nitroso-R-salt.

(4) Where the amount of nitroso-R-salt solution (0·2%) is increased to more than 1·0 ml, increase the amount of bromine water as follows:

Nitroso-R-salt Solution, ml	*Bromine Water, ml*
1·0– 5·0	1·5
5·0–10·0	2·5
10·0–12·5	3·5

CONCLUSIONS

The direct absorptiometric procedure, using nitroso-R-salt, is suitable for the determination of 60 to about 2 ppm of cobalt in titanium, zirconium and many of their alloys.

In the presence of titanium, permissible alloying constituents include manganese (20%), aluminium (10%) or iron (5%), and in the presence of zirconium amounts up to at least 5% of lead, aluminium, iron, manganese, zinc, magnesium, or tungsten. Interference by amounts up to 20% of tin or molybdenum, 5% of copper, chromium or vanadium, or 2·5% of nickel, can be overcome by simple modifications to the procedure, as described in the Method.

The procedure is simple, rapid, and particularly suitable for control analysis of reactor-grade zirconium, where the limit of cobalt is usually less than 20 ppm.

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Zusammenfassung—Es wird ein direktes Verfahren zur Erfüllung des Bedarfs einer Methode für die Bestimmung von Kobalt über der Reihe 2 bis ungefähr 50 Teile pro Million in Titan, Zirkon und Legierungen, entwickelt. Dieses Verfahren gründet sich auf der Bildung eines orange-farbigen Kobalt/Nitroso-R-Salz-Komplexes in einer Lösung von kontrollierter Acidität (cirka pH 6). Hydrolyse der Salze bei diesem pH wird durch den Zusatz von Ammonium-fluorid verhindert. Probieren hat gezeigt, dass bei Anwesenheit von Titan, bis zum mindesten 20 proz. von Mengen, 10 proz. von Aluminium oder 5 proz. von Eisen keinen Einfluss haben. Bei Anwesenheit von Zirkon stören bis zum mindesten 5 proz. Blei, Aluminium, Eisen, Mangan, Zink, Magnesium oder Wolfram nicht.

Einfache Modifikationen des Verfahrens eliminieren die Interferenz von Zinn oder Molybdän bis 20 proz. Kupfer, chrom oder Vanad bis 5 proz. oder Nickel bis 2,5 proz.

Das Verfahren ist einfach, rasch und für die Untersuchung des reaktorgradigen Zirkon besonders geeignet worin die Nachweisgrenze von Kobalt gewöhnlich weniger als 20 Teile pro Million ist. Die Standard-Abweichung in dem Gebiet von 20 Teilen pro Million ist cirka 0,3 Teile pro Million.

Résumé—Pour supléer au manque d'une méthode de dosage du cobalt, dans les limites comprises

entre 50 et 2 ppm près, dans le titane, le zirconium et leurs alliages, on a mis au point un procédé d'absorptiométrie directe. Ce procédé est basé sur la formation d'un complexe cobalt/sel nitroso R de coloration orangée, dans une solution d'acidité controlée (de pH 6 près). Pour empêcher l'hydrolyse des sels à ce pH on ajoute du fluorure d'ammonium.

Des expériences ont montré qu'en présence de titane jusqu'à 20% au moins de manganèse, 10% d'aluminium ou 5% de fer n'ont aucun effet; et qu'en présence de zirconium, jusqu'à 5% au moins de plomb, d'aluminium, de fer, de manganèse, de zinc, de magnésium ou de tungstène ne gênent pas.

A l'aide de simples modifications du procédé on peut éliminer les perturbations dues à l'étain ou au molybdène jusqu'à 20%, celles dues au cuivre, au chrome ou au vanadium jusqu'à 5%, ou au nickel jusqu'à 2,5%.

Le procédé est simple et rapide, et convient surtout à l'examen du zirconium utilisé dans les réacteurs, où la limite du cobalt est d'habitude inférieure à 20 ppm. L'écart-type à la limite de 20 ppm est de 0,3 ppm près.

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THE CHELOMETRIC DETERMINATION OF COBALT AND IRON USING A FLUORESCENT END-POINT

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Summary—A fluorescent end-point detection has been applied to the determination of cobalt and iron with EDTA. Macro amounts of iron and cobalt may be titrated without interference from the colour of their EDTA complexes. The application of calcein as a ' 'metalfluorechromic indicator" in the author's opinion provides a more distinctive end-point than any metallochromic indicator so far described.

ETHYLENEDIAMINETETRA-ACETATE (EDTA) has been applied in many procedures for the determination of cobalt[1] and iron.[2] The applications have included direct titrations as well as back titrations with a variety of end-point detection methods.

The use of visual indicators for these titrations has been handicapped by the colour of the cobalt and iron complexes with EDTA. As a result the new indicators proposed for the determination of these elements have been restricted to relatively small amounts of both iron and cobalt. For example, the determination of cobalt using pyrocatechol violet as an indicator is restricted to 10–12 mg of cobalt per 100 ml of solution.[3] As a result the analyst is faced with the problem of increasing errors because of reduced sample weights, or of taking small aliquots from large volumes of solution.

This difficulty has been circumvented by using spectrophotometric or potentiometric end-points.[4] The potentiometric method (particularly with a mercury electrode[5]) is not handicapped by the colour of the EDTA complexes. These methods are precise and are suitable for occasional determinations; however, the plotting of spectrophotometric or potentiometric end-points is not desirable for rapid routine analyses.

In spite of the many indicators and methods available using EDTA, it is apparent that there is a need for a visual indicator which will function in highly-coloured solutions. The approach selected for this problem was a fluorescent end-point detection. The successful (although seldom used) application of fluorescent pH indicators for acid-base titrations in coloured solutions has not been extended to EDTA titrations. This is surprising since many of the indicators used in visual EDTA titrations have been synthesized by adding a chelating group to acid-base indicators.[6] The term "metallochromic[7] indicators" has been used to describe these indicators which are capable of forming complexes with metals with a resultant change in colour.

The only previous application of a fluorescent end-point for an EDTA titration is the use of morin for the determination of indium and gallium.[8]

Schwarzenbach and Sallman[6] have introduced the iminodiacetic acid group into acid-base indicators by the Mannich reaction. It appeared that a similar technique with fluorescent pH indicators would produce a series of fluorescent metal indicators.

The term "metalfluorechromic indicators" will be used in this and subsequent publications to describe a new class of metal indicators. This term will include organic compounds capable of forming a metal complex the formation of which is accompanied by a change in the intensity of fluorescence. A change in the colour of the fluorescence may also occur, but is not necessary for a material to be included in the class of indicators.

The investigation of metalfluorechromic indicators was initiated with the condensation product of fluorescein, iminodiacetic acid and formaldehyde. This material is available under the name Calcein.* Calcein was first used by Diehl and Ellingboe[9] for the direct titration of calcium with EDTA. It has been indicated that the end-point is better in diffuse light than in illumination of high intensity.[9] The colour change is from yellow-green to brown. Tucker[10] suggested that the titration be carried out in diffuse daylight and that the end-point was improved by the addition of thymolphthalein. The thymolphthalein was added to reduce the fluorescence of the indicator. In the titration of small amounts of calcium it has been noted that the fluorescence of the indicator causes some difficulty.[11] In no case has the fluorescence of the indicator under ultraviolet light been used as a means of detecting the end-point although it is the author's opinion that the colour change reported is actually the disappearance of fluorescence.

TABLE I. BACK-TITRATION OF EDTA USING CALCEIN WITH COPPER SOLUTION (.03M)

Sample No.	pH	*ml* EDTA	*ml* Cu*
1	4.8	10	9.85
2	4.8	10	8.85
3	4.8	10	9.82
4	4.8	10	9.87
5	9.5	10	9.82
6	9.5	10	9.86
7	9.5	10	9.87
8	9.5	10	9.86

* Average value using PAN: 10 ml of EDTA is equivalent to 9.86 ml of copper solution.

EXPERIMENTAL

A preliminary investigation of calcein under ultraviolet light revealed a brilliant green fluorescence similar to the fluorescence of fluorescein. It was also observed that the fluorescence of calcein was severely quenched by the addition of copper and that the fluorescence reappeared on the addition of an excess of EDTA. This phenomenon was examined over a pH range of 4.5 to 9.5. It was apparent that calcein functioned as a metalfluorechromic indicator sensitive to copper ions.

The possibility of using calcein for the back-titration of an excess of EDTA with a copper solution was examined by preparing a 0.03M solution of copper and an approximately 0.03M solution of EDTA. The equivalent volumes of the two solutions were determined first using PAN in the conventional manner and then using calcein as a metalfluorechromic indicator. The results are shown in Table I. Several of the values in Table I using calcein were obtained in solutions to which

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an inert dye had been added in sufficient quantity to render the determination of the end-point by a metallochromic indicator impossible.

The indicator was first applied to iron and cobalt because of the limitations in determining macroamounts of these elements using metallochromic indicators. All of the titrations were carried out with a General Electric H100BLB4 bulb as the sole source of illumination.

Procedure:

To a slightly acid sample solution of cobalt or iron add somewhat more than the equivalent amount of EDTA and buffer to a pH of approximately 4.8 with sodium acetate-acetic acid. Dilute to 100 ml with water, add 1 drop of calcein indicator solution (0.1% in 0.001N sodium hydroxide), and back-titrate under ultraviolet illumination with a standard copper solution (0.03M). The end-point is detected by the extinction of the brilliant green fluorescence of the free indicator. The results of the titration of cobalt and iron are shown in Table II.

TABLE II. DETERMINATION OF COBALT AND IRON USING CALCEIN

Sample No.	*mg* Co Added	*mg* Co Found	Sample No.	Fe Added	Fe Found
1	62.28	62.25	13	23.95	24.03
2	62.28	62.25	14	23.95	24.07
3	62.28	62.16	15	23.95	24.05
4	62.28	62.29	16	23.95	24.03
5	72.66	72.65	17	47.90	47.98
6	72.66	72.65	18	47.90	47.88
7	72.66	72.72	19	47.90	47.87
8	72.66	72.58	20	47.90	47.93
9	72.66	72.61	21	76.95	76.96
10	83.04	83.08	22	76.95	76.95
11	83.04	82.90	23	76.95	76.96
12	83.04	82.94	24	76.95	76.90

DISCUSSION

After the end-point there is a residual fluorescence which is considerably less intense than that from the free indicator. The quenching of the fluorescence at the end-point is quite spectacular particularly with dark solutions and gives the appearance of a light being turned off. The approach to the end-point is similar to that with conventional indicators, with the exception that the local excess of copper is distinguished by a quenching of the fluorescence instead of the normal colour change in the region where the copper enters the solution.

The iron-EDTA complex absorbs so strongly in the ultraviolet that the ultraviolet penetrates only to a depth of about 1 cm with 50 mg of iron per 100 ml present. As a result the end-point is observed near the surface of the liquid. This presents no difficulty in the titration, particularly if the surface area is increased by increasing the vortex with rapid stirring.

This situation does not exist in the back-titration of cobalt. The fluorescence of the free indicator is apparent throughout the solution even with 80 mg of cobalt per 100 ml of solution. The cobalt titration may be carried out with equal accuracy in ammoniacal solution.

The weak residual fluorescence in the solution at the equivalence point may be caused by a contamination of fluorescein as well as by the copper-indicator complex.

New metalfluorechromic indicators and other applications will be the subject of subsequent investigations.

Zusammenfassung—Es wird eine fluoreszierende Endpunkt-Nachweis-Methode zur Bestimmung von Kobalt und Eisen mittels ÄDTA angewandt. Man kann Makromengen von Eisen und Kobalt ohne Interferenz von der Farbe ihrer ÄDTA-Komplexe titrieren. Der Meinung des Verfassers nach, gibt die Anwendung von Calcein als ein „Metall-Fluorchromer-indikator" einen unterschiedenderen Endpunkt als irgend ein bisher beschriebener Metallochromer-Indikator.

Résumé—Une méthode dans laquelle la fin de la réaction est mise en évidence par fluorescence a été appliquée au dosage du cobalt et du fer par l'EDTA. Le titrage de macro-quantités de fer et de cobalt peut s'effectuer sans que les colorations des complexes avec l'EDTA gêent. C'est l'avis de l'auteur que l'application de la calcéine comme "indicateur métal-fluorechromique" permet une fin de réaction plus distinctive que tout indicateur métallochromique décrit jusqu'ici.

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THE DETERMINATION OF ALUMINIUM, TITANIUM AND NICKEL IN THEIR ALLOYS

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Summary—An ion-exchange method for the separation of aluminium, titanium, and nickel is described. Aluminium, titanium and nickel are absorbed on a cation-exchange column which is coupled with an anion-exchange column. A $0.8M$ hydrofluoric–$0.06M$ hydrochloric acid mixture elutes aluminium from both columns, transfers titanium to the second column and leaves nickel in the first column.

The method, which is applied to a permanent magnet alloy, also gives an improved ion-exchange method for the separation of mixtures of nickel, aluminium, cobalt, copper and iron which eliminates a preliminary separation of copper.

A metalfluorechromic indicator is used to facilitate the titration of an excess of EDTA for the determination of those elements which form highly coloured complexes.

THE separation and determination of aluminium and titanium in complex alloys presents considerable difficulty in metallurgical analysis. Hydrogen sulphide or ammonium hydroxide precipitations to separate other elements from aluminium and titanium are associated with the usual problems of co-precipitation, post-precipitation and occlusion. This work was initiated to investigate ion-exchange resins as a means of separating aluminium and titanium from each other as well as from other elements.

Ion-exchange resins have been successfully applied for the separation of aluminium and nickel from cobalt and iron.[1] Kraus *et al.* have studied the absorption characteristics of titanium in hydrochloric acid medium on a strongly basic anion-exchange resin. Their results indicate that titanium will be present in the nickel-aluminium fraction obtained by eluting with a strong hydrochloric acid solution.

Aluminium and nickel in the same solution may be determined conveniently by employing a back-titration of an excess of EDTA with a standard copper solution.[1] The sum of the equivalents is obtained at the first end-point. The equivalents of aluminium are obtained from the second end-point after masking with fluoride in order to release an amount of EDTA equivalent to the aluminium present. The application of masking agents is convenient for chelometric titrations; however, the selective masking of one element in an aluminium-titanium solution has not been solved.

Ion-exchange methods were examined as a means to provide a convenient separation of aluminium and titanium. Freund and Miner[3] successfully separated aluminium from zirconium on a strongly basic anion-exchange resin using a hydrochloric-hydrofluoric acid medium ($0.06M$ HCl–$0.8M$ HF). Aluminium is eluted and zirconium is retained on the column.

In view of the similarity in the absorption characteristics of zirconium and titanium in hydrochloric acid medium[2,4] and formation of stable fluoro-complexes with both elements, this acid mixture was employed to separate aluminium from titanium. Preliminary experiments were confined to ascertaining that titanium was completely adsorbed on a strongly basic anion-exchange resin while eluting aluminium with the acid mixture described above. Synthetic mixtures of aluminium and titanium were prepared from standard solutions and passed through the column. Four column-volumes of the acid mixture were collected and checked for the presence of titanium by evaporating to fumes of sulphuric acid and adding hydrogen peroxide. Titanium was not detected in the eluate.

The application of this separation to actual alloys was difficult because the aluminium-nickel-titanium fraction from a previous ion exchange separation ($7M$ hydrochloric acid) was difficult to adjust to the proper acid mixture ($0.06M$ HCl–$0.8M$ HF).

This difficulty was removed by using a cation-exchange column connected before the anion-exchange column (Fig. 1). The eluate from a previous separation or a simple solution can be evaporated to a small volume and diluted to approximately 1 molar in hydrochloric acid. Aluminum, titanium and nickel are absorbed on a strongly acidic cation-exchange resin and the excess hydrochloric acid is removed by washing with water. Upon elution with $0.06M$ HCl–$0.8M$ HF, nickel remains on the cation-exchange resin, titanium is transferred to the anion-exchange column and aluminium is collected in a beaker below the second column.

The procedure, given below for a permanent magnet alloy (35 Fe, 34 Co, 14.5 Ni, 7 Al, 4.5 Cu and 5 Ti), also has been applied to nickel-base alloys containing 1 to 5 per cent of aluminium and titanium by treating the solution of the sample in the same manner as the aluminium-titanium-nickel fraction from the ion-exchange separation. The columns (Fig. 1) were prepared from six inch lengths of 1/2 inch polyethylene tubing (D). The polyethylene fittings (4) on the ends of columns were attached conveniently by "welding" sections of polyethylene hose connectors to the main portion of the columns by means of a heated glass cane. The resin is supported by a layer of teflon shavings (G). The reservoirs (A) are made from polyethylene bottles with a dropping bottle cap (B) inserted through a rubber stopper.

EXPERIMENTAL

Procedure

Dissolve a 0.5 g sample in *aqua regia* and evaporate to a syrupy consistency several times to remove nitric acid. Transfer the solution to an anion-exchange column (1 inch ID + 16 inches long) containing 80 g of a strongly basic anion-exchange resin (Dowex 1 × 8, 200–400 mesh, Cl^- form) with $7M$ hydrochloric acid. Elute the aluminium, nickel and titanium with 100 ml of $7M$ followed by 50 ml of $5M$ hydrochloric acid, the cobalt with $5M$ hydrochloric acid (complete removal of the blue cobalt band), the copper with $3M$ hydrochloric acid (complete removal of the lower yellow band) and the iron with $0.5M$ hydrochloric acid. Evaporate each fraction to about 5 ml and proceed as follows:

Cobalt and iron fractions: Transfer to a 100-ml volumetric flask and dilute to volume with water. To a 10-ml aliquot in a 250-ml beaker add approximately 100 ml of water, an excess of EDTA and one drop of calcein W* indicator (0.1 % in water), and adjust the pH to approximately 4.8 (NaAc–HAc buffer). Back-titrate the excess of EDTA with a standard copper solution to the quenching of the brilliant green fluorescence of the indicator, using ultraviolet light as the sole source of illumination.[5]

Copper fraction: Transfer to a 100-ml volumetric flask and dilute to volume with water. To a 10-ml aliquot add approximately 150 ml of water, an excess of EDTA and one drop of calcein W solution, and adjust the pH with an appropriate buffer. (The titration of copper may be conducted at pH values between 4.5 and 10.) Back-titrate the excess EDTA with a standard copper solution to the quenching of the fluorescence.

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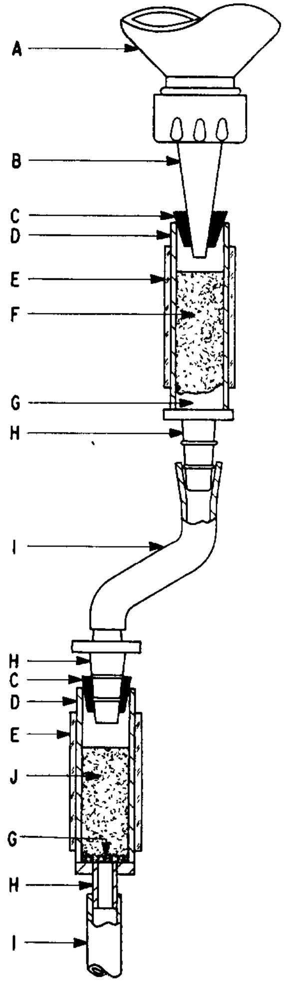

FIG. 1. Polyethylene ion-exchange columns in series

A—polyethylene bottle
B—dropping bottle cap
C—rubber stopper
D—½″ × 6″ polyethylene tubing
E—glass tubing
F—cation-exchange resin (strong acid)
G—Teflon shavings
H—polyethylene hose connector
I—Tygon tubing
J—anion-exchange resin (strong base)

Nickel, aluminium and titanium fraction: Add sufficient water (with stirring) to make the solution approximately 1 molar in hydrochloric acid and transfer the solution to the cation-exchange column. Rinse the sample on to the resin with 1 molar hydrochloric acid and wash with 25 ml of water. Couple the columns in series (Fig. 1) and elute with 150 ml of $0.8M$ HF–$0.06M$ HCl. After this elution, the aluminium is in the beaker (polyethylene) below the second column, all of the titanium is in the second column and all of the nickel is in the first column. Disconnect the columns and elute titanium from the second column with 150 ml of $3M$ hydrochloric acid (polyethylene). Wash the first column with water until the eluent is neutral (to remove fluoride) and elute the nickel from the first column with 50 ml of $4M$ hydrochloric acid.

Evaporate the aluminium and titanium fractions to fumes of sulphuric acid to remove fluoride ion. Add 25 g of ice to the aluminium fraction and an excess of EDTA, buffer to a pH of approximately 4.8 and heat to 90–100°. Add one drop of calcein W indicator and back-titrate the excess EDTA with a standard copper solution to the quenching of the fluorescence. The titanium fraction is treated in an identical manner as aluminium, except that 3 drops of 30-vol. per cent hydrogen peroxide are added immediately after the addition of ice and the solution is not heated.

The nickel fraction is evaporated to a small volume and nickel determined as described above for cobalt. Table I contains the values obtained on a permanent magnet alloy containing titanium.

TABLE I. ANALYSIS OF A PERMANENT MAGNET ALLOY CONTAINING TITANIUM*

Al Nominal	Al Found	Ni Nominal	Ni Found	Co Nominal	Co Found
7.90	8.00	14.7	14.69	34.3	34.41
7.90	8.00	14.7	14.72	34.3	34.30
7.90	8.01	14.7	14.69	34.3	34.33
7.90	7.94	14.7	14.72	34.3	34.32
7.90	8.07	14.7	14.65	34.3	34.30

Fe Nominal	Fe Found	Cu Nominal	Cu Found	Ti Nominal	Ti Found
33.4	33.44	4.00	3.96	4.80	4.80
33.4	33.49	4.00	4.02	4.80	4.74
33.4	33.47	4.00	3.93	4.80	4.77
33.4	33.45	4.00	4.08	4.80	4.70
33.4	33.49	4.00	3.93	4.80	4.68

* Nominal values determined by classical wet analysis and previously established ion-exchange methods. Values are given in weight per cent.

DISCUSSION

The column separations do not require close supervision during the elutions. The flow rates for the separations of the aluminium, titanium and nickel fraction are adjusted to about 1 drop every seven seconds with a pinch clamp on the Tygon tubing. The flow rate during the initial column separations of the sample solution is determined by the back pressure of the resin.

The titanium determination with EDTA in the presence of hydrogen peroxide may be carried out with PAN as an indicator as previously described;[5] however, the end-point is easier to detect with calcein W under ultraviolet illumination.

Zusammenfassung—Eine Ionenaustauschermethode zur Trennung von Aluminium, Titan and Nickel wird beschrieben. Die drei Ionen werden an einem Kationenaustauscher absorbiert, der mit einer Anionenaustauschersäule kombiniert ist. Eine Mischung 0.8 m in Fluss- und 0.06*M* in Salzsäure eluiert Aluminium von beiden Säule, bewegt Titan vom Kationit zum Anionit and lässt Nickel an der ersten Säule unbeeinflusst. Die Methode, zur Analyse einer Legierung für permanente Magneten angewandt, gibt auch eine verbesserte Austuaschermethode zur Trennung der Mischung Ni—Al—Co—Cu—Fe ohne vorhergehende Abscheidung von Kupfer.

Calcein unter UV Licht wird als Fluorescenc-Indicator bei EDTA-titrationen benützt und erleichtert die Endpunktserkennung beim Arbeiten in Lösungen mit stark gefärbten Komplexen.

Résumé—On décrit une méthode de séparation de l'aluminium du titane et du nickel sur résine échange d'ions. L'aluminium le titane et le nickel sont absorbés sur une colonne échangeuse de cations qui est couplée avec une colonne échangeuse d'anions. Un mélange d'acides chlorhydrique

0,06 M et fluorhydrique 0,8 M élue l'aluminium des deux colonnes, transporte le titane dans la 2ème colonne et laisse le nickel dans la première colonne.

La méthode qui est appliquée à un alliage magnétique permanent, fournit aussi une méthode améliorée sur échange d'ions pour la séparation de nickel, aluminium, cobalt, cuivre et fer, méthode qui élimine une séparation préliminaire du cuivre.

Un indicateur metallofluorochromique est utilisé pour faciliter le titrage d'un excès d'EDTA pour la détermination de ces éléments qui forment des complexes fortement colorés.

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THE HISTORICAL DEVELOPMENT OF THE PUBLIC ANALYST AND HIS WORK IN GREAT BRITAIN*

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Summary:—The development of early equipment used in food testing together with early legislation and examples of adulteration are described. A very brief history of the Society for Analytical Chemistry is given and the work of the present-day public analyst is outlined.

THE direct predecessors of investigators and discoverers in every branch of natural science were the public magicians of primitive society. These were a number of men set apart for the express purpose of benefiting the whole community by their skill, whether this skill was directed to healing, climatology or prophesy. In the higher stages of savagery this body of men were relieved from earning their livelihood (by this I mean they were paid fees in kind which saved them from being herdsmen, cultivators or warriors) and they were expected and encouraged to research into the ways of nature. It was their duty to learn the properties of the solar system, drugs and minerals, and the mysteries of life and death, so that solutions of problems presented to them by members of their communities could be found.

To maintain a show of knowledge was essential, as an error might well cost a witch doctor his life; hence in order to conceal their ignorance they practised imposture, and at the same time they were supplied with a powerful motive to substitute real for sham knowledge. The institution of this class of man has been of good service to humanity, as out of such poor and feeble beginnings have come the beneficial results of later ages.

Many primitive tribes, even now-a-days, have a fear that magic may be wrought on a person through the remains of his food, hence food residues are burned, buried or otherwise destroyed. This had the good effect of causing people to destroy refuse which if left to rot might have proved a source of disease. This custom has also strengthened bonds of good faith, as obviously no one who intended to harm a person by working magic on his food would himself partake of that food, lest by sympathetic magic he should suffer equally with his enemy from any injury done to the refuse. This sympathetic bond however only lasts while the food is actually in the stomach of each of the parties.[1]

The Kosher dietary laws[2] may be a natural development from these elementary attempts at hygiene, and cover the method of slaughtering an animal, preparation of the carcase and the prohibition of the use of certain animals such as rabbits, swine, etc. The law also covers personal cleanliness and it is a tribute to its efficiency that the Food Handlers' Bye Laws of many British Cities today are based on these ancient Biblical laws. One wonders if the prohibition of the consumption of rabbits was based

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* Paper read at a Symposium on the History of Analytical Chemistry, organized by the Midlands Section and the Western Section of the Society for Analytical Chemistry, and held at Shrewsbury on 16-17 May 1958.

on experience as it must be remembered that rabbits consume belladonna and are not poisoned by it but store the alkaloid in their liver in an amount sufficient to be toxic to humans who may partake of this organ.

Fire was also a purifying agent by consumption of noxious elements, and as its use developed it was employed in the Middle Ages for the consumption of, or protection against evil, *i.e.* by burning of "witches" or as a protection against wild beasts and robbers.

This latter point is a more positive approach to the subject and it is paralleled, in the case of food and its sophistication, by the appointment of Court Tasters. These persons essentially proved the absence of poisons, but the approach was also of value for distinguishing between poor and good quality foods.

Food legislation in this country first appeared about Norman times and is most readily traced in London, which is amongst the best documented of our local authorities. Thus in 1319 William Spurling of West Ham was convicted of selling two carcases of meat which had died of disease and the punishment was to be placed in the pillory while the condemned carcases were burned beneath him. It was also forbidden to sell by candle light as the rather dim illumination favoured substitution of inferior foods.[4]

In Tudor times, the Court of Aldermen of the City of London controlled retail prices. The City Livery Companies were also empowered to act on behalf of the City, and because of the importance of spices and their necessary use during this period as preservatives, the Freemen of the Mystery of Grocers were given the exclusive privilege of "garbling" spices and some drugs. The word[5] was originally a mediaeval commercial term meaning to sort out in order to separate what was good from the refuse. This meaning of the word is now obsolete but by perversion it now means to select, chiefly from speeches or literary works some portion which twists or renders ineffective the meaning of the author or speaker. Grocers received fees for their duties and confiscated any consignments which were adulterated or of bad quality.

In a similar way the Fishmongers Company, after their formation in 1536, controlled the condition of fresh and salted fish.

Bread formed a considerable part of the diet of those days, and there were many regulations governing the weight and price of bread although no mention is made of adulteration as we understand it today.

Ale and beer were most important beverages and "ale-conners" were appointed to taste each brew of ale and report on it to the Mayor before it was sold. An early ordinance concerning quality control applied to wines and ales is preserved in London Guildhall, and was issued by Dick Whittington when he was Lord Mayor in 1419.

Beer and ale of those days deteriorated rapidly hence a search had to be made for a method of preservation and this led to the introduction of hops, which preserved because of their resinous bitter principles. Ale-conners had to rely on informers and a search of suspected premises for many of their prosecutions, and it has also been claimed that they relied on a primitive test for the presence of sugar. Some of the suspected beer was spilt on to a wooden seat and the ale-conner sat down on it in his leather breeches. After a while, if he found his breeches sticking to the seat, the brewer was accused of adding sugar. A notable ale-conner for Stratford-on-Avon was Shakespeare's father. Even today the City of London, and Hungerford[6] in Berkshire, appoint ale-tasters, but their duties are mainly ceremonial.

During the seventeenth century adulteration became rife and took the form of additions of dust, sand and sweepings to tea, or of cheap herbs to spices. It was however during this period that the foundations of scientific means of detection were laid by Robert Boyle, who invented the hydrometer which later came to be used for the detection of water in milk, wine, etc. He defined analysis as being the recognition of individual substances in the presence of one another.

With the increasing commercialism of the eighteenth century, there was a considerable deterioration in food quality. Bread was baked with alum to increase the size and improve the colour of the bread made from inferior flour; tea was coloured with ferrous sulphate; chalk was added to bread in larger quantities than is practised at present. Tests for adulteration of bread and other foodstuffs were described in a pamphlet *An Essay on Bread, wherein the Bakers and Millers are vindicated from the Aspersions contained in Two Pamphlets* published in 1758 and written by H. Jackson, Chemist.

During this period the best milk in London was obtained from cows grazing in St. James's Park, and milk was often sold direct from the udders of cows driven around the street for that purpose; certainly the risk of watered milk was lessened by so purchasing it rather than buying from milk-maids who carried it in open pails. This latter milk was often described as "blue" referring to the colour of this diluted milk.

A report on the County of Lancashire, of this period contains a reference to a lactometer invented by a Mr. Dicas which determined the goodness of milk. Another adulterant referred to was Spanish Arnotta, now known as annatto, which was added as a colouring to Cheshire cheese.

Vinegar was subject to considerable sophistication and, according to Jackson's treatise, was prepared from oil of vitriol, coloured with burnt sugar or infusion of oak chips. Another custom to which Jackson drew attention was the use of copper sulphate to improve the colour of green vegetables.

He, Jackson, also referred to the risk of lead being removed from the glaze of earthenware by the use of acid liquids such as vinegar. Tests for metallic contamination were described and included the placing of a clean steel knife blade in the suspected foodstuff and noting the colour of any deposit—red for copper and blue-grey for lead.

The adulteration of beer continued, the use of ferrous sulphate, soap lye and other means of reducing the acidity of beer occurred, and again we have to thank Jackson for a description of the tests used, as he applied a decoction of galls and obtained a black colour when iron salts were present.

A factory actually existed in London at this time for the manufacture of faked wines, commencing with raisins which were fermented, followed by the addition of various colours and flavouring agents to produce the wine of choice. Lead, in the form of the acetate, was used to sweeten a wine and, in the form of litharge, to reduce the acidity.

Delicate chemical tests for lead were described by J. F. A. Göttling in a treatise called *A Portable Chest of Chemistry* published in 1791.

The alcoholic strength of spirits was controlled by a copper hydrometer invented by Clarke who published the description in the *Philosophical Transactions of the Royal Society*, 1729–1730, Volume 36.

The early years of the nineteenth century saw a further considerable increase in adulteration but a sensation was created by Accum, who exposed the extent of this adulteration by publishing, in 1820, a *Treatise on the Adulteration of Food and Culinary Poisons*. He quoted from the *Second Book of Kings, chapter* 4, *verse* 40—There is death in the pot[3]. I consider it is incorrect to take these words from their context and wish to refer to the preceding and succeding verses 39 and 41.

v. 39. *And one went out into the field to gather herbs, and found a wild vine, and gathered thereof wild gourds his lap full, and came and shred them into the pot of pottage; for they knew them not.*
v. 40 *For they poured out for the men to eat; and it came to pass, as they were eating of the pottage, that they cried out and said, O thou man of God, there is death in the pot. And they could not eat thereof.*
v. 41. *But he said. Then bring meal; and he cast it into the pot; and he said, Pour out for the people that they may eat. And there was no harm in the pot.*

The wild gourds were probably melon pumpkins and the flavour was no doubt due to an acrid resin obtained from the seeds which were used in the Levant as a taenicide. The addition of meal, probably barley, as a demulcent corrected the taste and enabled this local concoction to be consumed. An alternative suggested by Graves[7] is Colocynth or the bitter apple, also known as a wild gourd; but only minimum doses would be consumable as it is a purgative and a strong poison whose effects would not be neutralised by the meal of *verse* 41.

In spite of heavy fines, such as £150 for the use of ferrous sulphate in beer, adulteration continued in the early eighteen hundreds, but in 1848 another book appeared written by John Mitchell called *Treatise on the Falsifications of Food and the Means employed to detect them.* Following this, the *Lancet* in 1850 appointed an Analytical and Sanitary Committee to enquire into and report on the quality of solids and liquids consumed by all classes of the public. Dr. Hassall was one of the Commissioners appointed, and was responsible for the chemical analyses.

Hassall reported in 1855, and the revelations were so disturbing that a Select Parliamentary Committee was set up in the same year under William Schofield, Member of Parliament for Birmingham. This resulted in the passage of the first Food and Drugs Act in 1860. This Act, by virtue of half-hearted administration, became a dead letter, and only six or seven analysts were appointed. The most active of these analysts was probably Dr. Cameron of Dublin, who in 1862 examined 2,600 samples and found 1,500 adulterated. He secured 342 convictions.

Hassall was also the author of a book *Adulteration Detected*[8] in which he defined adulteration as the "intentional addition to an article for the purpose of gain or deception of any substance or substances, the presence of which is not acknowledged in the name under which the article is sold".

Hassall used the microscope widely, and in this book he described and illustrated genuine and spurious vegetable structures which could be identified by its use.

In 1872, the first Foods and Drugs Act was amended and enforcement was improved, but coincident with this the malefactor improved his knowledge and cleverly frustrated detection; thus, knowing that a lactometer was used by the analyst, a crafty dairyman could decrease the gravity of milk by the addition of water and then remove some fat to bring the gravity back within the normal range; and it was not until chemical means of estimating the true amount of fat was introduced that this fraud was checked.

The existence of natural variation in the composition of milk led to an escape or

"Appeal to Cow" clause in the Act, still operative today; it enables a farmer to prove a valid defence against a charge of adulteration, if he can produce milk from cows in his herd of the same low quality as that upon which the prosecution was based.

Up to this point, the analyst has been considered as only concerned with the analysis of foods and drugs, but during the 1860's Sir Edward Frankland laid the foundations of modern methods of water analysis and showed that many water supplies were polluted by decaying animal and vegetable matter—thus water examination was added to the duties of the public analyst.

About this time, scientific societies in the United Kingdom began to be organised, and in 1874 the Society of Public Analysts was formed with 27 members. The first general meeting was held in 1875 and there was a membership of 70 for the annual general meeting in 1876, whilst in the Jubilee year (1935) there were 500 members.

In the beginning the Society published accounts of its meetings in *Chemical News* but soon became a publishing body and printed *The Analyst.* Because of this duality of publication there are two volumes covering the first year of the Society. The early volumes of *The Analyst* make most interesting reading as many of the original members were men of strong convictions and prejudices, and often of uncertain and hasty temper; thus the early deliberations of the Society have not been the model exhibitions of polite deference shown nowadays.

In 1906 the title of the Society was altered to include "and other Analytical Chemists," the new title being more descriptive of the membership of the Society at that time.

Dr. Stephenson, the renowned Home Office Analyst and author of several editions of Taylor's Principles and Practise of Medical Jurisprudence, was an early member of the Society; and due to his interests and work on toxicology, he developed many delicate tests and improvements in technique for the examination for poisons in viscera. The analysts of those days used to undertake the work which is now done in the various Home Office Forensic Science Laboratories in the United Kingdom, although the public analyst may still be called on by the defence.

During the seearly formative years, the Society was continuously confronted with criticism, especially with regard to the competence and integrity of public analysts and the fact that reference of disputed analyses to the Somerset House Laboratory (now known as the Government Laboratory) was regarded as an injustice to men of standing, as the reputation of these men might be at the mercy of a Government subordinate of no greater competence and possibly of lesser calibre and experience.

Relations between public analysts and the Government Laboratory have however been most cordial, and this is, in some measure due to the high standard of training and qualification insisted upon by both parties. The need for an authority to test this competency was a major factor leading in 1877 to the formation of what is now known as the Royal Institute of Chemistry of Great Britain and Ireland.[9]

A Select Committee of the British House of Commons in 1894 suggested that the production of a recognised diploma or certificate should be required for the recognition of persons suitably trained as public analysts and the Council of the Institute of Chemistry established a special examination known familiarly as "Branch E."

In 1954 the public analysts in the Society formed an Association of their own for the better regulation of their professional duties and at this time the Society altered its name to the Society for Analytical Chemistry and became a true learned Society.

It is perhaps opportune to describe the present position of the public analyst and the work he does.

The public analyst[10] is appointed by a Local Authority, and his appointment, remuneration and the termination of the appointment are subject to agreement with the Minister of Agriculture, Fisheries and Food. A Local Authority is either a County, a County Borough or an Urban District with a population over 40,000. Nowadays the public analyst may be either a full time officer of the Authority working in a laboratory provided by the Authority, or a part-time officer working in his own laboratory and able to accept private work providing this work does not conflict with the interests of the Local Authority.

The analyst does not obtain his own samples although in past years this was done in a few cases, but the samples are now obtained by officers appointed by the Authorities. These sampling officers may be Public Health Inspectors, Inspectors of Weights and Measures, or in some places Police Constables. If the samples are taken in conformity with the Food and Drugs Act, then they are formal samples and are divided into three parts at the place of sampling and are sealed. One part of this sample is left with the vendor, the second part goes to the analyst, whilst the third portion is retained as a reference sample and may be sent on the instructions of a Court to the Government Chemist for analysis.

Samples may also be purchased in the normal manner of business and sent to the analyst. These are informal samples and no legal action can be taken on the results so obtained, but they may be used for routine control and to indicate commodities which may require subsequent formal sampling. Finally a private citizen has the right to have a sample examined and may either take the sample direct to the public analyst who will examine it on prepayment or to the Public Health Department who will pass it on to the analyst.

The type of sample sent for examination varies enormously. Thus in a county there are more milk samples taken than in an Urban Area where prepacked foods predominate. This is reflected in the figures for adulterated samples; for example in an Urban Area for which I act, in one recent quarter there were no adulterated samples but in an adjacent Rural Area for the same quarter, 3.9% of the samples were adulterated and this was due entirely to watering of milk.

The figures for adulteration in the last sixty years show the striking changes which have occurred since control has been enforced. Thus in 1892, 12.4% of samples taken in England and Wales were adulterated and in 1938 this had dropped to 3.7%. Due to war time shortages and the pecuniary advantages obtaining from sophistication, there was an increase during that time and this has not yet returned to the previous low level because of the many Statutory Instruments and Food Labelling Orders which have been promulgated during and since the war.

The trend in legislation from prohibitive to permissive is nowhere more marked than with colouring matters as at one time certain colours were prohibited on account of toxicity but now a few colours of various shades are recommended. The colours themselves must conform with high standards of purity.

Public analysts are often holders of appointments as Official Agricultural Analysts to enforce the quality and standards of animal feeding stuffs and of fertilizers under the appropriate legislation. This side of the work is most important when one remembers that out of something like three hundred and fifty thousand vegetables species in the world only about six hundred are cultivated and used by mankind, hence the value of encouraging the small number of plants required by the human race.

The analyst usually acts as scientific adviser to his local Authority and in this connection controls the quality of such diverse matters as swimming-bath water and sewage effluents, water treatment and river pollution, paints and lubricating oils, detergents and concrete construction.

A recent field for development is the analysis of rainwater from deposit gauges and of the atmosphere for sulphur dioxide, to assess atmospheric pollution, to assist the Local Authority in controlling it by persuading domestic fuel users to burn smokeless fuel, and to advise industrial concerns to install various safeguards against discharge of noxious matters.

The most recent extension of the work of the public analyst is into the field of radioactivity, and involves the examination of imported canned fish, effluents from hospitals and research establishments, and advice on such matters as siting of nuclear energy electric generating stations with regard to effect on adjacent industries or habitations.

As will be realised from what has already been said the public analyst may often find himself as a witness in Court.[11] His prime function here is to provide the Bench with the necessary technical foundation for judgment and this may be done either by instructing the solicitor or barrister or by giving evidence himself. In either case there must be complete frankness and understanding between counsel and expert; the real points of the case must be decided and then these points are the basis for concentration and development. It is thus essential carefully to prepare and wisely to select relevant material so that the witness can answer a question immediately and without ambiguity.

A Magistrates' Court may accept the certificate of a public analyst for a formal sample taken under the Foods and Drugs Act although the form of the certificate is often challenged, and recently it has been contended that the analyst is exceeding his duty if he states that a label is false or misleading.

My own view, and this is shared by my colleagues, is that the analyst is the one person who is in a position to help the Court on this point, in the light of his analysis, and in view of training and experience.

Shakespeare might have been describing the public analyst so well when he wrote "Each man in his time plays many parts;" at the same time the analyst does not "seek the bubble reputation" although being a lover of good food he may be like the justice—"of fair round belly and with good capon lined." The present day analyst does seek the co-operation of the citizen in endorsing the standards of purity required and thus influencing the food manufacturer and technologist.

Zusammenfassung—Die Entwicklung der im Nahrungs-probieren gebrauchten frühen Apparate, zusammen mit früher Gesetzgebung und mit Beispielen von Fälschung werden beschrieben. Eine sehr kurze Geschichte der Society for Analytical Chemistry wird auch angegeben, und die Arbeit des heutigen Staats-Analytikers wird skizziert.

Résumé—On décrit le développement des appareils utilisés autrefois dans l'analyse des aliments, la législation à cette époque et des exemples d'adultération. On présente ensuite une courte histoire de la Society for Analytical Chemistry, suivie d'un aperçu sur le travail de l'analyste public à l'heure actuelle.

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PHOTOMETRIC DETERMINATION OF GALLIUM USING MALACHITE GREEN*

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Summary—A selective and sensitive extraction-photometric determination of gallium using Malachite Green is described. The method permits the determination of as little as 0·001% of gallium in bauxites, zinc ores, and ashes without preliminary separations. After the isolation of gallium by ether extraction even smaller amounts can be determined.

INTRODUCTION

ALTHOUGH gallium has been estimated[30] to be present in the earth's crust to the extent of $1{\cdot}5 \,.\, 10^{-3}\%$ it does not form minerals of its own and occurs only very sparsely in nature. In minerals and ores gallium accompanies compounds of aluminium, zinc, and iron from which it is transferred to pig iron and aluminium during technological procedures. African germanite[11] and ashes[5] were found to possess the highest gallium content (1–2%).

The trace character of gallium requires sensitive methods for both its detection and its determination. For this reason much attention has been paid, apart from spectrochemical methods, to its colour and fluorescence reactions. Based on the position of gallium beneath aluminium in the third group of Mendeleeff's periodic table and on the resemblance of gallic salts to those of aluminium, some useful reactions of gallium with reagents used already for the detection or determination of aluminium have been discovered.

Nearly all of the colour and fluorescence reactions described up to now can be divided into several groups with respect to the reagents used: reactions using reagents of the aluminon type, using oxine and flavone derivatives, and using anthraquinone, azo and xanthene dyes.

Aluminon, the ammonium salt of aurintricarboxylic acid, was employed by Carey[3] for the detection, and by Molot and Kulberg[17], and Rinck and Feschotte[26] for the photometric determination of gallium. Kulberg[12] recommends the use of alumocresone (the ammonium salt of trimethylaurintricarboxylic acid) as an improved reagent of the aluminon type.

Sandell utilized the fluorescence reaction of gallium with oxine (8-hydroxyquinoline) for detection[28] of the element, and elaborated the first fluorometric method for its determination[29]. Hollingshead[10] uses 2-methyl-5-nitroso-oxine for his qualitative test, Ladenbauer and Slama[14] determine gallium by the use of dibromoxine (5:7-dibrom-8-hydroxyquinoline) which is more sensitive than oxine. Other halogen derivatives are described by Golovina and Alimarin[8] as well as by Nishikawa.[19]

Beck[1] applies morin (3:5:7:2′:4′-pentahydroxyflavone) for a qualitative fluorescence test; Bradacs, Feigl, and Hecht[2] extract the morin-cupferron complex and

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* I wish to express my thanks to Mr. Harry Matschina, Prague for the translation of the present paper.

determine gallium fluorometrically. Michal[16] uses chromatography followed by quercetine (3:5:7:3′:4′-pentahydroxyflavone) for the detection of gallium.

Poluektov[24] employed alizarin (1:2-dihydroxy-anthraquinone) and Pietsch[23] quinalizarin (1:2:5:8-tetra-hydroxyanthraquinone) for the detection of gallium. The latter dye was used by Willard and Fogg[32] in the first photometric determination of gallium.

The fluorescence reactions of gallium with azo dyes were first studied by Radley[25] who recommends, of about ten Solochrome dyes tested especially, 6 BFA Black (4-sulpho-2-hydroxy-α-naphthalene-azo-α-naphthol) and AS Black (4-sulpho-5-nitro-2-hydroxy-α-naphthalene-azo-α-naphthol) for the detection of gallium. Ladenbauer, Korkisch and Hecht[13] then developed a fluorometric determination based on the reaction of gallium with Solochrome Red ERS (4-sulpho-β-naphthol-α-azo-1-phenyl-3-methyl-5-hydroxypyrazol) and WDFA Black. Nazarenko and Vinkoveckaya[18] describe a fluorometric determination with sulphonaphtholazoresorcinol (1:3-dihydroxybenzene-[4-azo-1-]-2′-naphthol-4′-sulphonic acid). Lukin and Zavarichina[15] investigated the colour reactions of gallium with condensation products of H-acid and diazotised substituted *o*-amino-phenols and selected, from 12 derivatives, 2-hydroxy-3-chloro-5-nitro-benzene-(-1-azo-2′-)-1′-hydroxy-8′-amino-naphthalene-3′:6′-disulphonic acid, called Gallion, as the most suitable for its photometric determination.

The colour and fluorescence reactions of gallium with Rhodamine B in benzene extracts were utilized by Onishi[20] for its detection, and later by Onishi and Sandell[21] for its determination. More efficient extraction agents are described by Saltykova and Fabrikova[27] as well as by Culkin and Riley[4]. Ščerbov and Ivankova[31] determine gallium by the use of Rhodamine 6 G.

Among other reagents which do not belong to any group described previously may be mentioned salicylidene-*o*-amino-phenol used by Patrovský[22] for a qualitative fluorescence test, and pyrrolidine-dithiocarbamate as proposed by Geilmann, Bode, and Kunkel[7] for a nephelometric determination.

In the present work the reactions of gallium with some triphenylmethane dyes have been investigated. After preliminary tests Malachite Green was selected.

EXPERIMENTAL

Apparatus

All photometric measurements were carried out with a K 56 Koucký grating spectrophotometer using cylindrical cells of about 12 mm inner diameter.

Reagents

Gallium stock solution: 0·1344 g of gallic oxide (Johnson, Mathey and Sons, London) was dissolved with warming in 10 ml of sulphuric acid (1 : 1) and the excess of acid was fumed off. The residue was taken up with hydrochloric acid (1 : 1); the resulting solution was transferred to a volumetric flask of 100-ml capacity and made up to volume with acid of the same strength. From this stock solution containing 1 mg of Ga per ml the working solution containing 1 μg of Ga per ml was prepared by the successive dilution with hydrochloric acid (1 : 1).

Hydrochloric acid (p.a.): concentrated (s.g. = 1·19) and diluted (by volume) 1 : 1 and 1 : 3.

Titanous chloride (pure; Lachema): A 15% solution as purchased. (By analysis the acidity of the solution was found to be 4·6*N* with respect to hydrochloric acid).

Malachite Green (*tetramethyl-di-*p*-diamino-fuchsoniumchloride*): 2 g of the dye (Malachite Green B; Lachema) as the chloride (*i.e.*, a red powder; not the green metallic crystals of the oxalate) was dissolved under stirring in a mortar in 100 ml of hydrochloric acid (1 : 3). The resulting solution was filtered and stored in a dark bottle.

Diisopropylether (p.a. Lachema): The commercial product was freed from peroxide by shaking with potassium permanganate[21] and stabilised by the addition of diphenylamine as follows: 500 ml of ether was shaken three to four times in a 1-litre separatory funnel with 50 ml of a 2% solution of potassium permanganate in 2*N* H_2SO_4, and finally with three 50-ml portions of water. The ether thus freed from peroxide (a sample of the ether must not develop the yellow coloration of the peroxy compound on shaking with an acidified solution of a titanic salt) was shaken with 250 ml of hydrochloric acid (1 : 1) and stabilized by the addition of 0·01 g of diphenylamine per litre. The ether was stored in a dark bottle.

RESULTS

It was found that with Malachite Green in strong hydrochloric solution gallium yields a bluish-green complex which can be extracted with organic solvents. The reaction has to be performed in a reducing medium since the coloured oxidation product of the dye is also extracted under the conditions to be described. To maintain a reducing medium titanous chloride was used. The coloured complex of gallium was extracted with benzene, in which the dye is not soluble under the conditions described.

Determination of the maximum of absorption

The maximum of absorption of the coloured compound of gallium with Malachite Green was determined by measuring the dependence of the extinction on the wave-length (Fig. 1). All other measurements were carried out at maximum absorption, *i.e.* at 660 mμ.

Effect of concentration of hydrochloric acid

A solution having an acidity of 2·4*N*–8*N* with respect to hydrochloric acid and containing gallium, titanous chloride, and the dye was extracted with benzene. The extinction readings are plotted in Fig. 2 from which it can be seen that optimum extinction is attained if the acidity of the aqueous phase is 6·0*N*–6·5*N* with respect to HCl. All subsequent measurments were carried out in about 6*N* HCl which roughly corresponds to dilute hydrochloric acid 1 : 1.

Influence of concentration of the dye

To 5 ml of a solution containing gallium, titanous chloride was added followed by the addition of a 2% solution of Malachite Green (in hydrochloric acid 1 : 3) in amounts ranging from 0·1 to 3 ml, and the acidity of the solution was adjusted with hydrochloric acid to be optimal. The extinction readings are plotted in Fig. 3. It is obvious that the extinction increases with increasing amount of reagent, rapidly at first, but slowly later. As the extinction is not substantially increased by further addition of the reagent, 2 ml of a 2% solution of the reagent were used in all subsequent measurements.

Stability of coloration

The stability of the coloured complex of gallium with Malachite Green was investigated by measuring its extinction at regular intervals. The coloration was found to be stable for 3 hours after which the extinction gradually decreased.

Effect of number of extractions on the coloured complex

A solution having a total volume of 8·5 ml and containing gallium, the dye and the other reagents in their optimum amounts was extracted with several 5-ml portions of benzene. The extraction coefficient was computed from the readings

$$\frac{(\mathrm{Ga})_{\text{benzene}}}{(\mathrm{Ga})_{\text{aqueous phase}}} = 2{\cdot}74$$

From this rather low coefficient it can be seen that the sensitivity of the method is considerably decreased by repeated extraction, apart from the difficulty of a quantitative extraction with a solvent lighter than the aqueous phase. The coloured complex was, therefore, extracted only once with a 5-ml portion of benzene in all subsequent measurements. The volume of all reagents being kept constant, the obtained results were very reproducible.

Procedure

Transfer a 5-ml aliquot containing 0–5 μg of Ga in hydrochloric acid (1 : 1) to a dry 25-ml volumetric flask, add 1 ml of concentrated hydrochloric acid, 0·5 ml of a 15% solution of titanous chloride, stopper the flask with a rubber stopper and mix. After 5 minutes add 2 ml of a 2% solution of Malachite Green (in hydrochloric acid 1 : 3), mix well, add 5 ml of benzene, stopper the flask and shake for 2 minutes. After the separation of the phases transfer a portion of the benzene layer directly to a 1-cm photometric cell and measure the extinction at 660 mμ against benzene.

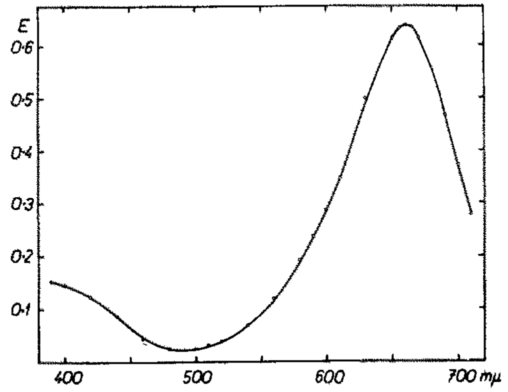

FIG. 1. Dependence of extinction upon wavelength.

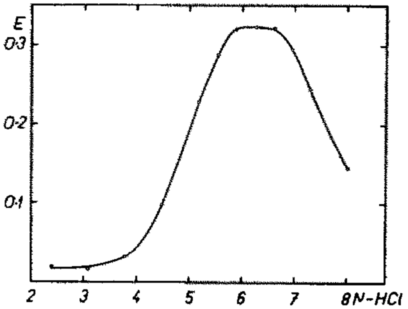

FIG. 2. Dependence of extinction upon acidity of the solution.

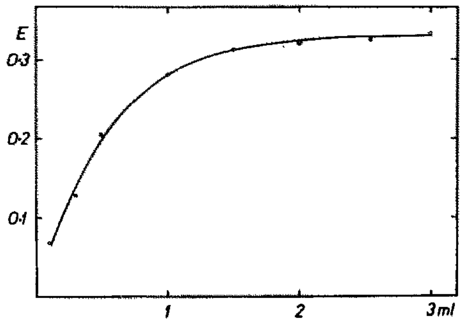

FIG. 3. Dependence of extinction upon amount of reagent added.

To obtain reproducible results the addition of all reagents used should be done precisely; *i.e.* by the aid of burettes and pipettes.

Calibration curve

For the construction of the calibration curve 0, 1, 2, 3, 4, and 5 ml of the gallium working solution containing 1 μg of Ga per ml (in hydrochloric acid 1 : 1) were used. The solution was made up to 5 ml with hydrochloric acid (1 : 1) and treated as described above. The calibration curve is shown in Fig. 4. The curve is slightly curved but quite reproducible.

Influence of foreign ions

According to literature data, extraction-colorimetric methods with Malachite Green have been described only for thallium[8] and antimony,[9] *i.e.* reactions developed in relatively feebly acid solution and not in a strong hydrochloric acid reducing solution. The influence of all available metals was therefore systematically investigated. Table I shows the results of the determination of 2 μg of Ga in the presence of a relatively large excess of a foreign element. These elements were added as the compounds in dilute hydrochloric acid solution (1 : 1) where shown in Table I. Occasionally, however, the solid compound was added directly to 5 ml of solution. In such case the increase in volume or the decrease in acidity—caused by the dissolution of the oxide—were neglected.

The formation of a sparingly soluble chloride (Ag), an element reduced to the metallic state by titanous chloride (Au, Pd, Se, Te), or a hydrolytic product (W) cause a difficult separation of the phases. Among the elements investigated, the following were found to yield a coloured extract: Cu, Mo, Sb, and Tl. However, under the conditions described their influence is small and permits the determination of gallium even in the presence of a 100- to 1000-fold excess of these metals. The element interfering most seriously is tin which causes markedly low results. In spite of this, however, gallium can be determined even in the presence of a 50-fold excess of tin. Table I shows only those results where the relative error induced by the foreign element did not exceed ±10%. Nitrates, as well as other oxidising agents, must, of course, be absent, since the coloured oxidation product of Malachite Green is extractable by benzene.

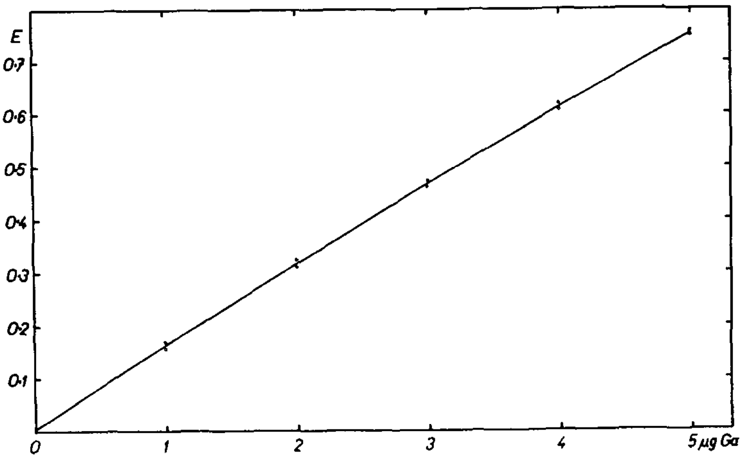

FIG. 4. Calibration curve of gallium with Malachite Green.

Practical application

Both the high selectivity and the sensitivity of the method permit the determination of gallium with Malachite Green in miscellaneous materials directly following decomposition *i.e.* without preliminary separations. If an aliquot corresponding to 25 mg is taken, as little as 0·001 % of Ga can be determined conveniently and with sufficient accuracy. The present method was used for the determination of Ga in bauxites, zinc ores, and ashes. The decomposition of these materials was accomplished as follows:

Decomposition of bauxites

Weigh 0·25 g of the finely ground sample into a platinum dish, ignite the sample in a muffle, treat with 1 ml of sulphuric acid (1 : 1) and about 5 ml of hydrofluoric acid, and fume off. Repeat the treatment with 1 ml of sulphuric acid (1 : 1) and about 3 ml of hydrofluoric acid and evaporate to dryness. The decomposition of ferric sulphate, however, must be avoided. Take up the residue with about 10 ml of hydrochloric acid (1 : 1), warm, transfer the resulting solution to a 50-ml volumetric flask by the aid of hydrochloric acid (1 : 1) and dilute to volume with acid of the same strength.

If need be, filter through a dry filter paper, and take a 5-ml aliquot for the determination.

Decomposition of ashes

Decompose 0·1 g of sample in the manner outlined above. Take up the residue with about 10 ml of hydrochloric acid (1 : 1), transfer the solution to a 500-ml volumetric flask and dilute to the mark with distilled water. For the determination take a 1–2 ml aliquot, add hydrochloric acid to attain

TABLE I. DETERMINATION OF 2 μg OF Ga IN THE PRESENCE OF FOREIGN IONS

Element	Amount of element *mg*	Form added	Ga found, μg	Deviation, μg	Relative error %
Ag[a]	10	Ag_2SO_4	1·95	−0·05	−2·5
Al	10	$KAl(SO_4)_2\cdot 12H_2O$	2·01	+0·01	+0·5
As	25	$Na_2AsO_4\cdot 7H_2O$	2·18	+0·18	+9
Au[b]	5	$HAuCl_4\cdot 4H_2O$	1·94	−0·06	−3
Ba	25	$BaCl_2\cdot 2H_2O$	1·98	−0·02	−1
Be	25	$BeSO_4\cdot 4H_2O$	2·01	+0·01	+0·5
Bi	25	$BiCl_3$	1·97	−0·03	−1·5
Ca	25	$CaCl_2$	2·07	+0·07	+3·5
Cd	10	$CdSO_4\cdot \frac{8}{3}H_2O$	1·97	−0·03	−1·5
Co	25	$CoCl_2\cdot 6H_2O$	2·07	+0·07	+3·5
Cr	25	$Cr_2(SO_4)_3\cdot K_2SO_4\cdot 24H_2O$	2·13	+0·13	+6·5
Cs	25	$CsCl$	1·96	−0·04	−2
Cu[c]	5	$CuCl_2$	2·15	+0·15	+7·5
Dy	3	Dy_2O_3	2·15	+0·15	+7·5
Er	4	Er_2O_3	2·07	+0·07	+3·5
Eu	10	Eu_2O_3	2·10	+0·10	+5
Fe	15	$FeCl_3\cdot 6H_2O$	2·01	+0·01	+0·5
Gd	10	Gd_2O_3	1·96	−0·04	−2
Ge	1·5	$GeCl_4$	1·96	−0·04	−2
Hf	5	K_2HfF_6	1·95	−0·05	−2·5
Hg	10	$HgCl_2$	1·89	−0·11	−5·5
Ho	10	$HoCl_3\cdot 6H_2O$	2·05	+0·05	+2·5
In	5	$In_2(SO_4)_3$	2·08	+0·08	+4
K	50	KCl	1·87	−0·13	−6·5
La	5	La_2O_3	1·92	−0·08	−4
Li	25	$LiCl$	1·92	−0·08	−4
Lu	4	Lu_2O_3	1·97	−0·03	−1·5
Mg	25	$MgSO_4\cdot 7H_2O$	1·91	−0·09	−4·5
Mn	25	$MnCl_2\cdot 4H_2O$	1·98	−0·02	−1
Mo	5	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	2·20	+0·20	+10
Na	50	$NaCl$	1·88	−0·12	−6
Nb	10	NbF_5	2·17	+0·17	+8·5
Nd	10	$NdCl_3\cdot 6H_2O$	1·90	−0·10	−5
NH_4	25	NH_4Cl	1·86	−0·14	−7
Ni	25	$NiCl_2\cdot 6H_2O$	2·09	+0·09	+4·5
Os	10	OsO_4	2·06	+0·06	+3
Pb	25	$PbCl_2$	2·13	+0·13	+6·5
Pd[b]	10	$PdCl_2$	2·09	+0·09	+4·5
Pr	10	$PrCl_3\cdot 6H_2O$	2·04	+0·04	+2
Pt	10	$PtCl_4\cdot 5H_2O$	1·85	−0·15	−7·5
Rb	25	$RbCl$	1·86	−0·14	−7
Rh	10	$RhCl_3\cdot 4H_2O$	1·96	−0·04	−2
Sb	5	$SbCl_3$	2·20	+0·20	+10
Sc	25	$ScCl_3$	2·11	+0·11	+5·5
Se[b]	10	SeO_2	1·96	−0·04	−2
Sm	10	$SmCl_3\cdot 6H_2O$	2·15	+0·15	+7·5
Sn	0·1	$(NH_4)_2SnCl_6$	1·98	−0·02	−1
Sr	25	$SrCl_2$	2·07	+0·07	+3·5

Table I (*continued*)

Element	Amount of element *mg*	Form added	Ga found, μg	Deviation, μg	Relative error %
Ta	10	TaF_5	2·17	+0·17	+8·5
Tb	10	$Tb_2(C_2O_4)_3$	2·15	+0·15	+7·5
Te[b]	5	TeO_2	1·94	−0·06	−3
Th	25	$Th(CH_3CO_2)_4$	2·18	+0·18	+9
Ti	25	$TiO(SO_4)$	2·00	±0·00	±0·0
Tl	0·5	Tl_2SO_4	2·06	+0·06	+3
Tm	10	Tm_2O_3	1·98	−0·02	−1
U	25	$Na_2U_2O_7$	2·18	+0·18	+9
V	10	NH_4VO_3	2·09	+0·09	+4·5
W	1	$Na_2WO_4\cdot 2H_2O$ (+50 mg NH_4F)	2·13	+0·13	+6·5
Y	10	$Y_2(CO_3)_3\cdot 3H_2O$	2·03	+0·03	+1·5
Yb	10	$YbCl_3\cdot 6H_2O$	2·01	+0·01	+0·5
Zn	25	$ZnCl_2$	1·91	−0·09	−4·5
Zr	25	$ZrOCl_2\cdot 8H_2O$	2·13	+0·13	+6·5
fluoride	50[d]	NH_4F	2·10	+0·10	+5
oxalate	50[d]	$(NH_4)_2C_2O_4\cdot H_2O$	1·89	−0·11	−5·5

[a] AgCl is precipitated in part.
[b] $TiCl_3$ reduces the metal to the elemental state.
[c] the colour caused by copper fades with time.
[d] weight of compound added.

a concentration of hydrochloric acid of 1 : 1, dilute to 5 ml with hydrochloric acid (1 : 1) and proceed as described above.

Decomposition of sulphide zinc ores

Decompose 0·25 g of the finely ground ore by the aid of 5–10 ml of reversed *aqua regia* and, if need be, add a few drops of bromine. Treat with 2 ml of dilute sulphuric acid (1 : 1) and evaporate to white fumes of the acid. Let cool, dilute with a few ml of water to remove nitric acid and evaporate to dryness. Treat the residue as described under bauxite.

If the gallium content of the sample is less than 0·001%, take up the residue of the decomposed sample with about 10 ml of hydrochloric acid (1 : 1)—an aliquot of the solution to be determined can be used instead—and isolate the gallium by ether extraction.

Isolation of gallium by ether extraction

To the solution to be examined add an excess of a 15% solution of titanous chloride (in most cases 2–5 ml will do) and adjust the acidity to about 7*N* with respect to HCl. After 5 minutes, extract with two equal portions of di*iso*propylether (the ether must not contain peroxide). Transfer the combined extracts to a small beaker, add 0·3 ml of a 10% solution of sodium chlroide and evaporate to dryness. Treat the residue with 5 ml of hydrochloric acid (1 : 1), warm until solution is complete, transfer to a volumentric flask of 10-ml capacity and dilute to mark with acid of the same strength. For the determination take a 5 ml aliquot.

The gallium content of the materials described was checked by the Rhodamine B method by the procedure of Saltykova and Fabrikova.[27] The measurements were carried out at 565 mμ.

As can be seen from Table II, the results obtained with various materials are quite reproducible and the gallium content found is in good agreement with the mean value of the check method.

TABLE II. DETERMINATION OF GALLIUM IN INORGANIC MATERIALS

No.	Sample	gallium found, %	
		with Malachite Green	with Rhodamine B
1	Bauxite	0·0008 0·0008 0·0007	0·0006
2	Bauxite	0·0026 0·0026 0·0026 0·0025 0·0026 0·0026	0·0025
3	Bauxite	0·0037 0·0036	0·0035
4	Ashes	0·86 0·89 0·87	0·87
5	Zinc Concentrate[a]	0·00037 0·00036	0·00036

[a] Gallium isolated by ether extraction.

DISCUSSION

Almost all colour and fluorescence reactions of gallium cited at the beginning of the present paper are developed in either neutral or feebly acid solution, and are therefore to be attributed to the reaction of the gallic ion Ga^{3+}. The reaction of gallium with Rhodamine B discovered by Onishi[20,21] is completely different since it is developed in strong hydrochloric acid solution (about 6*N* HCl) where gallium acts as the chlorogallic anion. Another xanthene dye Rhodamine 6 G, also exhibits a reaction similar to Rhodamine B, and this was investigated by Ščerbov and Ivankova.[31]

In preliminary tests it was found that in strongly acid solution gallium yields coloured complexes extractable by organic solvents not only with Malachite Green but also with other basic triphenylmethane dyes such as fuchsin, methyl violet, and crystal violet. Pentamethoxyl Red and the basic thiazinic dye, Methylene Blue give a similar reaction.

It can be presumed that in strong hydrochloric acid solution (about 6*N* HCl) gallium forms complex compounds also with other basic dyes, *i.e.* with such whose coloured part will act as the cation, bonding with chlorogallic acid, which fact may be a guide for the elaboration of further methods of this type.

Zussammenfassung—Ein selektives und empfindliches Extraktions-photometrisches Verfahren zur Bestimmung des Galliums unter Verwendung von Malachitgrün wird beschrieben. Das Verfahren ermöglicht die Bestimmung von bis zu 0·001% Gallium in Bauxiten, Zinkerzen und Flugstäuben ohne vorangehende Abtrennung. Nach Isolierung des Galliums mit Hilfe von Etherextraktion können noch kleinere Mengen bestimmt werden.

Résumé—L'auteur décrit un dosage photométrique par extraction sélectif et sensible du gallium utilisant le vert malachite. La méthode permet le dosage de quantités aussi faibles que 0,001% de gallium dans les bauxites, les minerais et les cendres de zinc, sans séparations préliminaires. Après isolement du gallium par extraction à l'éther, des quantités encore plus faibles peuvent être dosées.

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VISUAL EGTA TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM

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Summary—The successive visual chelometric determination of both calcium and magnesium has always involved a precipitation step for one of these metal ions. This step is eliminated by titration with the chelon, ethylene glycol-*bis*-(β-aminoethyl ether)-N:N′-tetra-acetic acid (EGTA), which chelates calcium selectively, and by using zincon as indicator with added zinc-EGTA as indicator sensitiser. Magnesium is then determined by titration with ethylene-(dinitrilo)-tetra-acetic acid in the same solution after adding potassium cyanide and Eriochrome Black T indicator. Mixtures of zinc, calcium and magnesium may be successively determined by a similar procedure where first the zinc is titrated with tetra-ethylenepentamine using zincon as indicator. The theoretical treatment of the large number of equilibria involved are represented in an easily digestible manner with the pY–pH diagrams.

THE chelometric determination of mixtures of calcium and magnesium has found wide application in the analysis of water, limestones, dolomites, magnesite, soils and physiological materials, and the numerous publications on this subject have been reviewed.[31]

In the most commonly used procedure the sum of calcium and magnesium in the mixture is first determined, then the calcium alone is determined on a second portion of the sample after masking the magnesium by precipitation. The titration of the total calcium plus magnesium with ethylene-(dinitrilo)-tetra-acetic acid (EDTA or H_4Y) is carried out in an ammonia buffer using Eriochrome Black T indicator.[26] In the second determination, the magnesium is precipitated as the hydroxide at pH 12.5 or higher, and the calcium is titrated with EDTA using as indicator: murexide,[5,14,27] calcon C.I. 202,[13] Erichrome Blue SE,[8] Acid Chrome Blue,[29] Patton and Reeder dye,[18] Calcein,[6] Palatin Fast Blue GGNA, Pr. 144,[24] Palatine (Calcofast Blue 2G) or Methylthymol Blue.[16] The disadvantage of this method occurs when the ratio of magnesium to calcium is one or greater because some calcium is always occluded in the precipitated magnesium hydroxide resulting in low values for calcium, and some indicator is absorbed on the precipitate, thus obscuring the end-point. Various procedures have been proposed for eliminating this source of error.[1–4,9–12,17,30]

Recently a potentiometric procedure which avoids chemical separation or precipitation was developed;[25] in this method ethylene glycol-*bis*-(β-aminoethyl ether)-N:N′-tetra-acetic acid (EGTA) is used as a selective chelating agent for titrating calcium in the presence of magnesium ion. In the present article a procedure is proposed for the visual titration of calcium and magnesium in mixtures containing large excesses of magnesium without employing chemical separation or precipitation. The calcium is first titrated selectively with EGTA. Mixtures of zinc, calcium and magnesium may be successively determined by a similar procedure where the zinc is first titrated with tetra-ethylenepentamine (tetren).

Selection of chelon and indicator

The difference in stability constants of the calcium and magnesium complex of EGTA (log K = 11.0 and 5.2, respectively) allowed the selective titration of calcium in the presence of magnesium with a potentiometric end-point using the mercury electrode.[25] This difference is also sufficient to allow a selective visual titration with indicator end-point, if the indicator meets certain requirements. First, the indicator under the titration conditions must not combine with magnesium; otherwise the colour change would be obtained only after chelation of *both* calcium and magnesium. Second, the indicator must change colour at a rather specified pCa.

At the present time, none of the commonly employed calcium indicators fulfill the first condition; on the contrary, they form even stronger complexes with magnesium than with calcium. Because of this lack of a specific calcium sensitive indicator, zincon (2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene),[15,23] sensitised by the addition of some zinc ion, was chosen as the indicator system. This procedure is analogous to the sensitisation of an end-point using α-(2-pyridylazo)-β-naphthol (PAN) or α-Naphthylazoxine with copper ion.

Fortunately zincon does not complex under the titration conditions with calcium and magnesium. With zinc, a reasonably stable blue complex is formed in the pH range from 8 to 10 and zincon has been used for the direct EDTA titration of zinc with a colour change from orange-yellow to blue.[15] When zinc-EGTA complex is added to an ammonical solution of calcium containing zincon indicator, the exchange

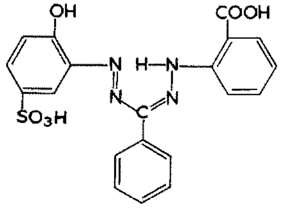
$$Ca^{2+} + \underset{\text{Orange-Yellow}}{HIn^{3-}} + ZnY^{2-} \rightarrow CaY^{2-} + \underset{\text{Blue}}{ZnIn^{2-}} + H^+ \qquad (1)$$

reaction takes place, and the solution turns blue. Upon titration with EGTA, the calcium is first chelated, and next the titrant reacts with the zinc-indicator complex, liberating the indicator and thus giving a colour change to orange-yellow. It is obvious that the zinc-indicator complex has to exhibit a rather specified stability: (*a*) reaction (1) must take place to a considerable extent with calcium but not with magnesium ion and (*b*) a sharp end-point may be obtained after the titration of calcium, *e.g.* EGTA must shift reaction (1) to the left readily. It may also be seen from equation (1) that the extent of the indicator reaction depends on pH and on the concentration of zinc-EGTA complex.

The numerous factors involved in the proper activation of an indicator response may be studied quantitatively from pY–pH diagrams.[20] The various pH dependent equilibria involved in reaction (1) may be represented in an easily digestible way in such a diagram and furthermore the optimal titration conditions, *i.e.* pH, buffer, concentration of activating metal ion, may be easily predicted. For the construction of such diagrams the stability constants of the metal-indicator and metal-chelonate complexes involved are required as well as the acidity constants of the chelon and indicator. The required constants, except for those of the indicator, were known. Consequently the next step involved the determination of the acidity constants and the zinc stability constant of zincon.

Determination of equilibrium constants of zincon

Acidity constants: Zincon (the monosodium salt) has three acid hydrogens: a carboxylic hydrogen, a phenolic hydrogen and a secondary amine hydrogen. Because of the lack of information in literature, an investigation of the acid-base properties has been attempted. The experimental investigation, however, was handicapped by the chemical instability of the dye.



From this study the ionisation stages of zincon may be summarised as follows:

$$\underset{\substack{\text{Pink}\\ \text{(decomposes)}}}{H_3In^-} \overset{pk_1=4}{\leftrightharpoons} \underset{\text{Yellow}}{H_2In^{2-}} \overset{pk_2=7.85}{\leftrightharpoons} \underset{\text{Orange-yellow}}{HIn^{3-}} \overset{pk_3=15}{\leftrightharpoons} \underset{\text{Violet}}{In^{4-}} \qquad (2)$$

The carboxyl hydrogen is lost at pH of about 4; however, the equilibria were not further investigated in more acidic medium because the dye decomposes rapidly in this region. Above a pH of 5 the dye is considerably more stable. Spectra of the dye at pH 5.9 and 10 are shown in Fig. 1, corresponding to the species H_2In^{2-} and HIn^{3-}. The pk_2 was obtained from absorbancy versus pH measurements at 460 mμ and found to be 7.85. Although the equilibrium is assumed to involve only one proton, a plot of log $[HIn^{3-}]/[H_2In^{2-}]$ versus pH gave a slope somewhat greater than one, this discrepancy being attributed to the poor stability of the indicator. The violet form of the totally ionised indicator is obtained only in about 10*M* sodium hydroxide.

Formation constant of zinc complex: An optical method was selected for the determination of the stability constant of the zinc-zincon complex although the use of a mercury electrode as a third order pZn electrode[21] may have been applicable. The procedure consists of measuring the absorbance of the complex for a solution containing the metal ion and the indicator over a wide range of pH. Because zinc is precipitated as hydroxide in the critical pH range, a complexing buffer (triethanolamine) was added to prevent precipitation and its complexing action was taken into account in the calculation. In an experiment where the pH of the solution was varied by dropwise addition of base, very poor results were obtained because of the decomposition of zincon under these conditions. Although somewhat better results were obtained when the pH was changed from the alkaline to the acidic side by dropwise addition of acid, the procedure finally adopted consisted of obtaining each point from a separate solution where the pH was adjusted prior to addition of indicator. Solutions containing $10^{-3}M$ zinc, $10^{-2}M$ buffer (acetic acid, pyridine or triethanolamine) were made up and a measured amount of indicator was added immediately before the measurement. In this way the effect of decomposition was minimised. The points obtained experimentally were corrected for the decrease in the zinc ion activity caused by the complexing properties of buffer. The correction factors were evaluated from the corresponding stability constants.[21] A plot of the log [metal-dye complex]/[dye] *vs.* pH gave a straight line with a slope of 2. The intersection with the abscissa occured at pH 6.4. The formula of the zinc-zincon complex was determined from photometric micro-titrations of the indicator with zinc and *vice versa*. The same end-point was obtained in both titrations, and the metal-zincon ratio was found to be 1 : 1.

The equilibrium measured in the pH variation study is thus

$$H_2In^{2-} + Zn^{2+} \rightleftharpoons ZnIn^{2-} + 2H^+ \tag{3}$$

and

$$K^{(1)} = \frac{[ZnIn^{2-}]\,[H^+]^2}{[H_2In^{2-}][Zn^{2+}]} \tag{4}$$

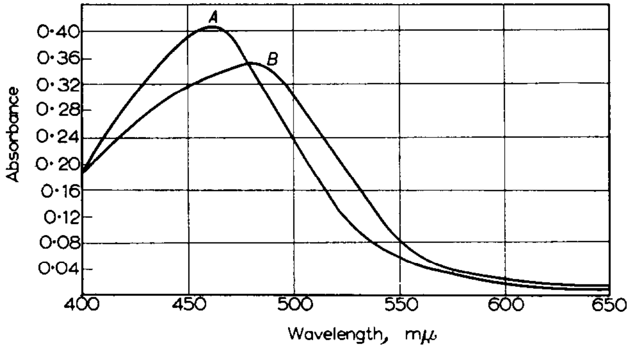


FIG. 1. Absorption spectra of free dye
A— 2 × $10^{-3}M$ zincon in acetate buffer pH 5.9.
B— 2 × $10^{-3}M$ zincon in triethanolamine buffer pH 10.0.

The constant $K^{(2)}$ for the equilibrium,

$$HIn^{2-} + Zn^{2+} \rightleftharpoons ZnIn^{2-} + H^+ \tag{5}$$

which is predominant above pH 8, is obtained by combining $K^{(1)}$ with the acidity constant k_2.

$$K^{(2)} = \frac{[ZnIn^{2-}]\,[H^+]}{[HIn^{2-}]\,[Zn^{2+}]} = \frac{K^{(1)}}{k_2} \tag{6}$$

The values evaluated from the experimental data are $10^{-9.8}$ for $K^{(1)}$ and $10^{-1.95}$ for $K^{(2)}$.

For verification, the constant $K^{(2)}$ was obtained in another way, by measurement of the equilibrium

$$HIn^{3-} + M^{2+} + ZnY^{2-} \rightleftharpoons ZnIn^{2-} + MY^{2-} + H^+ \tag{7}$$

Strontium and barium were selected for the metal ion M^{2+} because, in these cases, the position of equilibrium for the reaction may be determined colorimetrically in a pH range where the indicator is predominantly present in the form HIn^{2-}. Thus

$$K^{(3)} = \frac{[ZnIn^{-2}]\,[MY^{2-}]\,[H^+]}{[HIn^{-3}][M^{2+}][ZnY^{2-}]} = \frac{K^{(2)}K_{MY}}{K_{ZnY}} \tag{8}$$

Solutions $0.001M$ in M^{2+}, MY^{2-} and ZnY^{2-} were prepared, zincon was added, and the absorbancy of the zinc-indicator complex at 625 mμ was measured as a function of pH. The pH was changed from the alkaline to the acid side by dropwise addition of acid. The equilibrium point where $[ZnIn^{2-}] = [HIn^{3-}]$ occurred at pH 9.30 for strontium and at pH 9.35 for barium. From a knowledge[25,28] of the stability constants for the metal-EGTA chelonates ($K_{ZnY} = 13.0$, $K_{SrY} = 8.5$ and $K_{BaY} = 8.4$) values for $K^{(2)}$, of $10^{-1.8}$ and $10^{-1.75}$ were calculated. The agreement between these values and the one obtained by the first method ($10^{-1.95}$) must be considered satisfactory in view of the difficulties encountered.

Construction of pY–pH diagram

The construction and application of pY–pH diagrams has been discussed thoroughly elsewhere[20] and the discussion given here is restricted to the specific analysis of calcium by the proposed method. To illustrate the use of pY–pH diagrams for this system, consider Fig. 2.

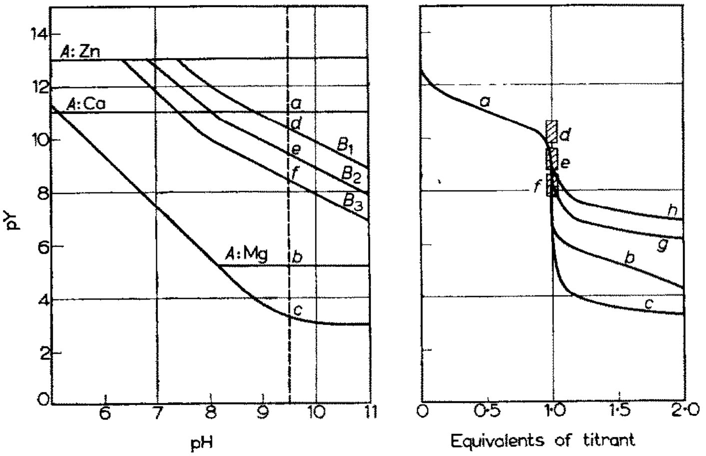


Fig. 2. pY–pH diagram and corresponding pY titration curve for the titration of $10^{-3}M$ calcium in the presence of magnesium with EGTA and zincon. Effect of buffer and hydrolysis of zinc disregarded. B_1, B_2 and B_3 correspond to Zn-EGTA in concentrations of 10^{-5}, 10^{-4} and $10^{-3}M$, respectively.

The lines in the diagram represent pY as a function of pH ($pY = -\log[Y]$ where [Y] is the concentration of the fully dissociated $EGTA^{-4}$) for the solution at different characteristic stages: at half titration, at the midpoint of the indicator colour change, and at 100% past the end-point.

The lines *A* in Fig. 2 correspond to the situation at half titration of the respective metal ion, *i.e.* to the pY of the solution containing equal amounts of free metal ion and metal-EGTA complex. The pY is then equal to the stability constant K_{MY} of the metal-EGTA complex.

$$pY_A = \log K_{MY} \tag{9}$$

In the presence of an auxiliary complexing agent or a complexing buffer (necessary to prevent hydrolysis of zinc and to maintain the desired pH), the metal ion activity is decreased. This is taken into account by the pH-dependent factor β.

$$pY_A = \log K_{MY} - \log \beta \tag{10}$$

The effect of buffer and hydrolysis has been neglected in Fig. 2 but is considered in Fig. 4.

The pY_B at 50% colour change of the indicator is represented by line *B*

$$pY_B = \log K_{MY} + \log \alpha_{In} - \log C_M - \log K_{MIn} \tag{11}$$

Equation (11) is obtained from the equations for the stability constant K_{MY} of the metal-chelonate and the effective stability constant, K'_{MIn}, of the metal-indicator complex.

$$K_{\mathrm{MY}} = \frac{[\mathrm{M}]}{[\mathrm{M}]\,[\mathrm{Y}]} \tag{12}$$

$$\mathrm{K}'_{\mathrm{MIn}} = \frac{[\mathrm{MIn}]\,[\alpha_{\mathrm{In}}]}{[\mathrm{M}]\,[\mathrm{In}]'} \tag{13}$$

$[\mathrm{In}]'$ represents the total analytical concentration of the unmetallised zincon in all ionisation stages.

Assuming that the colour change occurs at or very close to the equivalence point

$$[\mathrm{MY}] = C_{\mathrm{M}} \tag{14}$$

Furthermore, at the 50% colour change point

$$\mathrm{MIn} = [\mathrm{In}]' \tag{15}$$

Combining equations (12), (13), (14) and (15) and solving for [Y] gives equation (11).

Line *C* characterises the situation 100% past the end-point. The analytical concentration $[\mathrm{Y}]'$ of EGTA is then equal to the initial stoichiometric metal ion concentration C_{M}. According to the definition

$$[\mathrm{Y}]' = \mathrm{Y} \,.\, \alpha_{\mathrm{Y}}$$

where

$$\alpha_{\mathrm{Y}} = 1 + \frac{[\mathrm{H}^+]}{k_n} + \frac{[\mathrm{H}^+]^2}{k_n k_{n-1}} + \cdots \frac{[\mathrm{H}^+]^n}{\pi_n k_n} \tag{16}$$

and [Y] is the concentration of the totally ionised EGTA. The *k*'s are the acidity constants of EGTA. The pY at this point becomes

$$\mathrm{pY}_{\mathrm{C}} = \log \alpha_{\mathrm{Y}} - \log C_{\mathrm{M}} \tag{17}$$

Line *A* is independent of the metal ion concentration but lines *B* and *C* are dependent on metal ion concentration [see equations (10), (11), (17)].

The sharpness of the indicator colour change is completely characterised for any pH by two end-point indices:[20] Δ_1 and Δ_2. Δ_1 is equal to the pY difference between line *A* and line *B* and Δ_2 is equal to the pY difference between lines *B* and *C*.

$$\Delta_1 = \mathrm{pY}_{\mathrm{A}} - \mathrm{pY}_{\mathrm{B}} \tag{18}$$

$$\Delta_2 = \mathrm{pY}_{\mathrm{B}} - \mathrm{pY}_{\mathrm{C}} \tag{19}$$

Small end-point indices (2 or less) indicate somewhat dragging end-points whereas large end-point indices (3.5 or larger) indicate very sharp end-points. Δ_1 characterises the sharpness before the equivalence-point whereas Δ_2 characterises the sharpness after the equivalence-point.

Interpretation of pY–pH diagram

Consider a solution containing equal amounts of zinc, calcium and magnesium and some zincon indicator. When this solution is titrated with EGTA at a pH of 9.5, the pY starts at infinity, and then drops along the vertical dotted line as illustrated in Fig. 2. The zinc is titrated first, calcium second, then the indicator changes colour and finally the magnesium is titrated, but incompletely because its EGTA complex is very weak.

The relationship of the pY–pH diagram to a titration curve is shown in the right hand side of Fig. 2. The theoretical pY titration curve for $10^{-3}M$ calcium solution at pH of 9.5 is represented by *a–c*. The titration in the presence of an equal amount of magnesium is given by curve *a–b*. In the presence of a 10- or 50-fold molar excess of magnesium the curve follows *a–g* and *a–h*, respectively. Because zincon does not react with calcium, no colour change is obtained with this indicator in the absence of zinc ions. In the presence of zinc-EGTA complex, however, a colour change occurs. The pY at which the colour change occurs depends on the total zinc concentration and this dependency is extremely important. The 50% colour change at pH 9.5 is given in the pY–pH diagram by the points *d*, *e*, *f*, for $10^{-5}M$, $10^{-4}M$, and $10^{-3}M$ zinc present.

In an actual titration, however, it is in general not the 50% colour change point which is observed as the end-point. In the colour change of zincon from blue (zinc complex) to orange-yellow (free dye), the colour appears reddish purple from about 40% to 60%, then gradually changes to orange-yellow. The eye perceives the pure orange-yellow colour at about 80% colour change. Thus, the eye observes best a colour change between 40% and 80%. In the right side of Fig. 2, the pY region at which this change occurs is shown as a shaded area for $10^{-5}M(d)$, $10^{-4}M(e)$, and $10^{-3}M(f)$ total zinc present. Although the upper part of the pY titration curve will exhibit a somewhat different shape when large amounts of zinc-EGTA are present (and because of zinc hydrolysis), the shape of the curve the end-point will remain practically the same.

It is evident from Fig. 2, right, that an appropriate amount of zinc must be present in order that the colour change should occur at the equivalence point of the calcium titration. For example, in the titration of calcium alone, an amount of zinc corresponding to *f* will yield the best result. When less zinc is present, an early and dragging colour change would be obtained (*d*). The diagram also shows that the equivalence-point is shifted towards higher pY values when increasing amounts of magnesium are present in the solution. In order to obtain a correct end-point in this case, the colour change should also occur at higher pY values. This may be achieved experimentally by adding less zinc-EGTA to the solution and also by titrating until the appearance of the reddish tinge (upper end of shaded area) and not until the appearance of the full orange-yellow colour (lower end of shaded area). These principles were taken into consideration in the practical titrations of calcium-magnesium mixtures.

Factors influencing the end-point

From the pY–pH diagrams, it may be seen that the end-point of the titration of calcium is obviously influenced by the pH, the concentration of zinc-EGTA complex and the buffer concentration. These effects were studied more closely by photometric titrations under varying solution conditions.

Effect of buffer concentration: The influence of zinc hydrolysis and buffer was not considered in the discussion of Fig. 2. However, it must be realised that larger buffer concentrations may affect the titration curves and the end-point. Photometric titration curves for the titration of calcium at various concentrations of ammonia and triethanolamine buffer are shown in Fig. 3. The curves are not seriously affected by buffer concentrations up to $0.01M$. In the presence of $0.1M$ ammonia, however, a strong influence is exerted. These effects are readily explained from the pY–pH diagrams of Fig. 4.

According to equation (10), the pY of line *A* (corresponding to half-titration) is

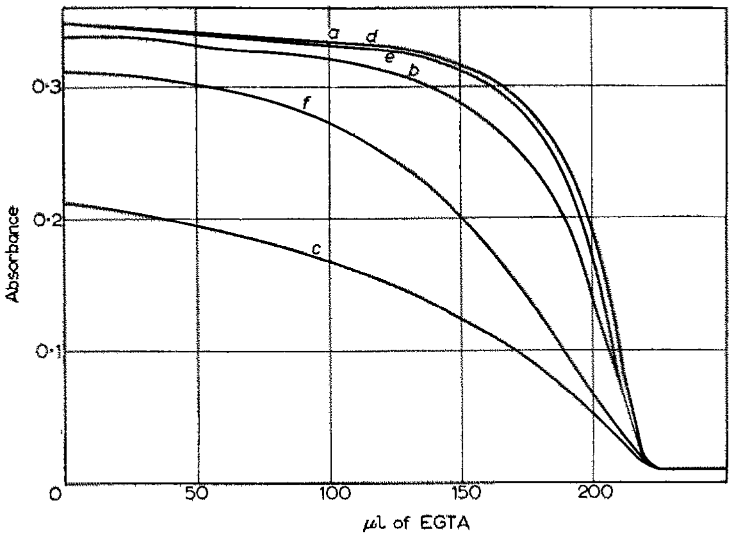


FIG. 3. Effect of buffer concentration. Spectrophotometric titration of 2.5×10^{-4} calcium with EGTA in the presence of $2.5 \times 10^{-4}M$ Zn-EGTA using zincon as indicator and different concentrations and types of buffers. *a*, *b*, and *c*: ammonia buffer pH 9.5, $10^{-3}M$, $10^{-2}M$ and $10^{-2}M$, respectively. *d*, *e*, and *f*: triethanolamine buffer pH 8.5, $10^{-3}M$, $10^{-2}M$ and $10^{-1}M$, respectively.

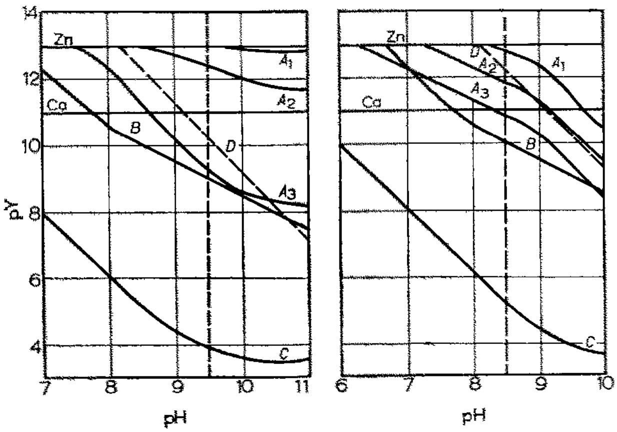


FIG. 4. Effect of buffer on titration of calcium 2.5×10^{-4} in the presence of and equal amount of Zn-EGTA. Left: ammonia buffer. Right: triethanolamine buffer. A_1 $0.001M$, A_2 $0.01M$, A_3 $0.1M$ buffer. B, 50% colour change of zincon. D, hydrolysis of zinc (oblique dashed line).

lowered by a complexing buffer. Fig. 4 illustrates the effect of ammonia and triethanolamine in various concentrations of the pY_A of zinc. Calcium does not form a complex of any appreciable stability with these reagents and the lines corresponding remain unaltered. It has been pointed out[20] that the sharpness of the colour change before the equivalence point is determined by the pY difference Δ_1 (end-point index) between line *A* for the metal ion to be titrated (or line *D* in case of hydrolysis) and line *B* for the sensitive indicator. In the present case the indicator is not directly sensitive to calcium ion, but is sensitised by the addition of zinc. Under such circumstances the end-point index Δ_1 is equal as a first approximation to the pY difference between line

A for the ion to be titrated *or* line *A* or *D* for the sensitising metal ion, *whichever is lower*, and line *B*. In the absence of a complexing buffer, Δ_1 is equal to the difference between line *A* for calcium and line *B* at pH 8.5 and between line *D* and line *B* at pH 9.5. Because of hydrolysis of zinc (oblique dashed line *D* in Fig. 4), sufficient buffer (when large quantities of zinc are present) must be added to cause the zinc hydroxide to dissolve; this means that the buffer line *A* must fall beneath the hydrolysis line *D*.

As long as line *A* for zinc is not depressed below line *D* or the line for calcium, complexation of zinc does not change the value of Δ_1 and thus does not affect the end-point sharpness to any considerable extent. This is practically the case with $0.001M$ or $0.01M$ ammonia at pH 9.5 or the same concentrations of triethanolamine at pH 8.5 (lines A_1 and A_2). The experimental findings of Fig. 3 are in accordance with the evidence from pY–pH diagrams. The photometric titration curves corresponding to the cases A_1 and A_2 for ammonia and triethanolamine are approximately identical. In a $0.1M$ buffer, however, line *A* drops considerably below line *D* or the calcium line and Δ_1 (pY difference between A_3 and B) becomes smaller. The sharpness of the photometric end-point is correspondingly less, particularly with $0.1M$ ammonia buffer (curve *C*, Fig. 3).

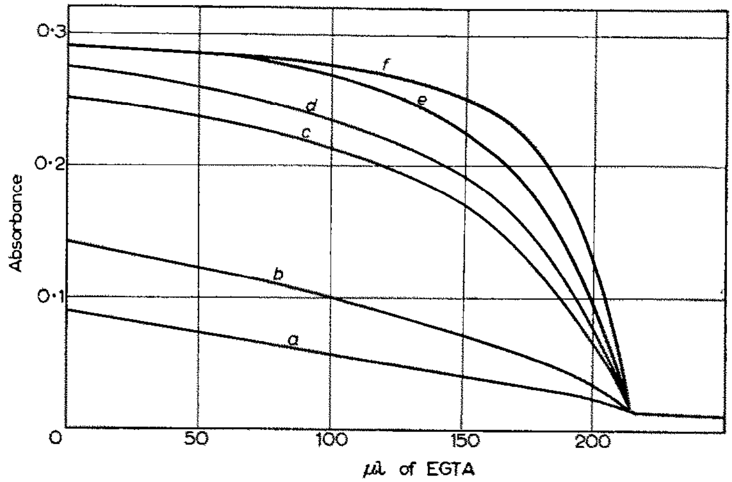


FIG. 5. Effect of concentration of Zn-EGTA. Titration of $2.5 \times 10^{-4}M$ calcium in $5 \times 10^{-3}M$ ammonia buffer. 1 ml $2 \times 10^{-3}M$ zincon. Concentration of Zn-EGTA: a- $5 \times 10^{-6}M$, b- $1 \times 10^{-6}M$, c- $2.5 \times 10^{-5}M$, d- $5 \times 10^{-5}M$, e- $1 \times 10^{-4}M$, f- $2.5 \times 10^{-4}M$.

Effect of Zinc Concentration: Fig. 5 illustrates the effect of increasing total zinc concentration on a photometric titration curve of calcium at pH 8.5 with zincon indicator. From 5×10^{-6} to 2.5×10^{-4} the sharpness of the colour change prior to the end-point increases gradually. The phenomenon is readily explained with the pY–pH diagram of Fig. 2. The distance between line *A* for calcium and the indicator line *B* increases with increasing zinc concentration and thus gives a better end-point index Δ_1. The corresponding decrease of Δ_2 does not show in the titration curve, because its value is very large (above 4) even at the highest zinc-EGTA concentration employed.

EXPERIMENTAL

Reagent and solutions:

Ethylene glycol-bis-(β-aminoethyl ether)-N:N′-tetra-acetic acid (J. R. Geigy, Chel DE), recrystallised: solutions were prepared by weighing an approximate amount required for 0.1*M* solution, and were standardised potentiometrically against zinc or calcium standard solutions using the mercury electrode[21,22,25] or metallochromic indicators.

Disodium dihydrogen ethylenediamine tetra-acetate (*EDTA*): standard solution. 37.225 g reagent grade disodium salt of ethylene (dinitrilo)-tetra-acetic acid dihydrate were dissolved in distilled water and diluted to 1 litre. The titre was checked against the primary standard calcium or zinc.

Stoichiometric Zn-EGTA solution: prepared by mixing 10 ml of 0.1*M* zinc solution with the equivalent of EGTA, neutralising with sodium hydroxide, and diluting to 100 ml.

Tetra-ethylenepentamine dihydrosulphate (*tetren*): the commercial product of Union Carbon and Carbide Chemicals Co. was purified and recrystallised according to Reilley and Holloway.[18] 3.855 g were weighed, dissolved in distilled water, and diluted to 1 litre. The solution was standardised potentiometrically against primary standard zinc solution using the mercury electrode.

Standard zinc solution: 8.138 g of freshly ignited zinc oxide (Reagent Grade) were dissolved in dilute nitric acid and diluted to 1 litre; 1 ml contains 6.538 mg of zinc.

Standard calcium solution: 5.608 g of freshly ignited calcium oxide (Reagent Grade) were dissolved in dilute nitric acid and diluted to 1 litre: 1 ml contains 4.008 mg of calcium.

Stock metal salt solutions: prepared by weighing the approximate amount of the nitrate salts (using high purity chemicals) required for 0.1*M* solutions and standardising against the different chelons potentiometrically using a mercury electrode or with metallochromic indicators.

Zincon (*2-carboxy-2′-hydroxy-5-sulphoformazyl benzene*): Baker Reagent, Lot No. 4054. A suitable solution of the indicator was prepared by dissolving 0.2 g in 5 ml of 0.1*N* sodium hydroxide and diluting with demineralised water to 100 ml. A few drops of this indicator solution used in the titration of zinc or calcium gave a sharp end-point.

Eriochrome Black T.: (F241-C1203). Solid indicator, finely ground with sodium chloride in the proportion of 1 : 100.

Buffer pH 8.5: dissolve 74.6 g triethanolamine in demineralised water, add the proper amount of nitric acid and dilute to 500 ml.

Buffer pH 9.5: dissolve 40 g of ammonium nitrate in 300 ml water, adjust to pH 9.5 by adding ammonium hydroxide and dilute to 500 ml.

Buffer pH 5.4: dissolve 41 g of crystalline sodium acetate in 200 ml demineralised water, adjust to pH 5.4 by adding acetic acid, and dilute to 500 ml.

PROCEDURE

Mixtures of calcium and magnesium

Mixtures of calcium and magnesium are neutralised with sodium hydroxide or hydrochloric acid to about pH 5.0, then the least possible amount of ammonia buffer pH 9.5 is added. Two to three drops of zincon indicator are added followed by stoichiometric zinc-EGTA dropwise until the solution is distinctly blue. The calcium in the sample is then titrated with standard EGTA to the point of maximum colour change per drop of titrant. It may be necessary to add additional drops of zincon before the end of the titration, as the indicator fades rapidly.

Potassium cyanide sufficient to mask the zinc and traces of copper (which would block the indicator) and then Eriochrome Black T sufficient to give a distinct wine-red colour are added. The magnesium in the sample is titrated with standard EDTA to a blue-grey colour. The titration must be carried out slowly in the region of the end-point and it may be advisable to add fresh quantities of potassium cyanide and Eriochrome Black T near the end-point. If traces of iron are present, they may be reduced at first with ascorbic acid, then masked by cyanide.

Mixtures of zinc, calcium and magnesium

The sample is neutralised roughly with sodium hydroxide or hydrochloric acid, then the ammonia buffer is added in the least quantity sufficient to hold the different metal cations in solution during the titration. Two to three drops of zincon indicator are added and the zinc is titrated with standard tetren solution to an orange-yellow colour. It is important not to add any excess of tetren after the

TABLE I. TITRATION OF CALCIUM IN THE PRESENCE OF MAGNESIUM

Molar ratio Ca : Mg	Taken *mg*	Found *mg*	Dev. %
1 : 0	5.080	5.078	−0.04
		5.080	±0.00
		5.081	+0.01
1 : 1	0.508	0.506	−0.40
		0.517	+1.75
		0.503	−0.90
	2.540	2.534	−0.23
		2.536	−0.16
		2.540	0.00
	5.080	5.087	+0.16
		5.070	−0.20
		5.082	+0.04
1 : 5	2.032	2.040	+0.40
		2.038	+0.30
		2.029	−1.15
	5.080	5.070	−0.20
		5.082	+0.04
		5.088	+0.16
1 : 10	2.540	2.540	±0.00
		2.534	−0.20
		2.538	−0.08
	5.080	5.083	+0.06
		5.085	+0.09
		5.092	+0.24
1 : 20	1.524	1.529	+0.26
		1.530	+0.40
		1.540	+1.10
	2.540	2.540	±0.00
		2.544	+0.16
		2.536	−0.16

TABLE II. TITRATION OF CALCIUM AND MAGNESIUM MIXTURES

Calcium			Magnesium		
Taken *mg*	Found *mg*	Dev. %	Taken *mg*	Found *mg*	Dev. %
4.007	3.996	−0.28	2.432	2.450	+0.74
	4.023	+0.40		2.413	−0.79
	4.004	−0.08		2.440	+0.33
	3.985	−0.08		2.424	−0.33
	4.010	+0.08		2.432	±0.00
	3.976	−0.52		2.428	−0.16
4.007	4.012	+0.13	12.160	12.17	+0.08
	3.993	−0.35		12.16	±0.00
	4.030	+0.58		12.09	−0.58
4.007	4.012	+0.08	24.32	24.23	−0.37
	4.023	+0.40		24.19	−0.54
	4.004	−0.08		24.32	±0.00
4.007	4.009	+0.05	48.64	48.62	−0.04
	4.016	+0.22		48.68	+0.08
	4.023	+0.40		48.70	+0.14
4.007	4.030	+0.58	121.60	121.60	±0.00
	4.024	−0.40		121.53	−0.06
	4.040	−0.83		121.70	+0.08

end-point is reached because it will replace the EGTA from zinc-EGTA, and correspondingly low results for calcium will be obtained.

Calcium and magnesium are subsequently determined according to the procedure described above.

RESULTS

The results obtained for the titration of calcium in the presence of various quantities of magnesium are listed in Table I. Samples containing 1 aliquot of calcium and 0, 1, 5, 10 or 20 aliquots of magnesium were titrated with EGTA and the results showed that these proportions of magnesium have little effect on the quality of the end-point. However, if the ratio of Mg : Ca is increased further, the clear orange-yellow colour of free zincon is not obtained at the end-point, but a persistent bluish tinge is observed. The end-point is considered to be the point of maximum sharpness of colour change.

The magnesium determination is carried out in the same solution at the same pH, using EDTA as titrant, ascorbic acid and potassium cyanide as masking agents, and Erichrome Black T as indicator. Owing to the complementary colour of zincon present in the solution, the end-point is blue-grey instead of pure blue. Results of successive calcium and magnesium determinations in the same solution are listed in Table II.

TABLE III. TITRATION OF ZINC, CALCIUM AND MAGNESIUM MIXTURES

Zinc			Calcium			Magnesium		
Taken *mg*	Found *mg*	Dev. %	Taken *mg*	Found *mg*	Dev. %	Taken *mg*	Found *mg*	Dev. %
1.308	1.301	−0.54	4.007	4.007	±0.00	2.432	2.428	−0.16
	1.308	±0.00		4.004	−0.07		2.432	±0.00
	1.312	+0.31		3.985	−0.55		2.428	−0.16
	1.307	−0.01		4.006	−0.02	12.160	12.150	−0.08
	1.305	−0.23		4.012	+0.12	48.600	48.600	±0.00
3.268	3.262	−0.18	4.007	4.004	−0.07	2.432	2.441	+0.37
	3.276	+0.26		4.024	+0.43		2.437	+0.21
	3.225	−0.40		4.016	+0.22		2.438	+0.25
	3.276	+0.24		4.012	+0.12	12.160	12.170	+0.08
	3.264	−0.15		4.007	±0.00	48.600	48.560	−0.08
6.538	6.524	−0.21	4.007	4.011	+0.10	2.432	2.441	+0.37
	6.550	+0.18		4.007	±0.00		2.437	+0.20
	6.538	±0.00		4.005	−0.05		2.423	−0.37
	6.538	±0.00		4.005	−0.05	12.160	12.170	+0.08
	6.542	+0.06		4.016	+0.22	48.600	48.580	−0.04
65.380	65.380	±0.00	4.007	4.012	+0.12	2.432	2.424	−0.32
	65.375	−0.07		4.016	+0.22		2.437	+0.20
	65.387	+0.01		4.002	−0.12		2.441	+0.37
	65.375	−0.07		4.002	−0.12	12.160	12.150	−0.08
	65.375	−0.07		4.024	+0.42	48.600	48.560	−0.08

Table III contains the results of the successive determinations of zinc, calcium and magnesium in the same solution. The results given in the tables for the zinc, calcium and magnesium illustrate the surprising possibility of determining the mentioned cations by taking the advantage of applying different chelons and indicators.

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Zusammenfassung—Durch Titration mittels Chelon, Äthylenglycol-*bis*-(β-aminoäthyläther)-N:N′-tetraessigsäure, das ein Calciumchelat selektiv bildet, und mittels Zinkon als Indikator kann man Calcium in der Anwesenheit von Magnesium bestimmen. Magnesium wird dann durch Titration mit Äthylen-(dinitrilo)-tetraessigsäure in der gleichen Lösung mit Eriochrom Schwarz T als Indikator bestimmt. Man kann Gemengen von Zink, Calcium und Magnesium auch durch ein ähnliches

Verfahren successiv bestimmen, worin Zink mit Tetraäthylenpentamin titriert wird. Die theoretische Behandlung der Gleichgewichte wird auf eine einfache Weise mit pY–pH Bilder angegeben.

Résumé—Le dosage successif, par chelométrie du calcium et du magnésium avec fin de réaction visuelle, a toujours fait intervenir un stade de précipitation pour l'un de ces ions deux métalliques. Ce stade est éliminé par le titrage avec le chelon, acide éthylène glycol bis (-aminoethyl ether)-N:N'-tétracétique (EGTA) qui complexe le calcium de manière sélective et en utilisant le zincon comme indicateur auquel on ajoute le complexe zinc-EGTA comme sensibilisateur. Le magnésium est ensuite dosé par titrage avec l'acide éthylène (dinitrilo)-tétracétique dans la même solution après addition de cyanure de potassium et de noir ériochrome T comme indicateur. Des mélanges de zinc, de calcium et de magnésium peuvent être successivement dosés par un procédé semblable: le zinc est d'abord titré avec la tétraéthylène pentamine en utilisant le zincon comme indicateur.

L'étude théorique du grand nombre d'équilibres mis en jeu est présentée sous une forme facilement assimilable avec les diagrammes pY–pH.

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DETERMINATION OF ALUMINIUM IN THORIUM OXIDE AND A SEPARATION SCHEME FOR INTERFERING IONS

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Summary—A method is presented for the separation and subsequent estimation of 0.5 to 150 μg of aluminium in thorium oxide which contains corrosion products of steel and other impurities. The aluminium is separated from thorium, iron, zirconium and some other elements by extraction of these elements with a hexone solution of thenoyltrifluoroacetone (TTA). Aluminium is then extracted with 8-quinolinol and chloroform in the presence of hydrogen peroxide, sodium cyanide, and nitrilotriacetic acid, which mask interfering ions that are not removed by the TTA extraction. In view of the effectiveness of the separation scheme in eliminating interferences, the aluminium can be measured either fluorometrically or spectrophotometrically, depending on the quantity to be determined. When the thorium oxide also contains manganese and cobalt, a double extraction, using TTA and sodium diethyldithiocarbamate, is required to remove the interfering ions before the aluminium can be successfully determined as the quinolinate.

INTRODUCTION

A METHOD was needed for the determination of microgram and sub-microgram quantities of aluminium in thorium oxide which contained a number of minor constituents, such as iron, nickel, chromium, manganese, cobalt, titanium, zinc, copper, and uranium. A review of the colorimetric methods for the determination of microgram quantities of aluminium[11] revealed that, while several methods do provide for the estimation of aluminium in thorium, none is entirely adequate for use when the thorium contains the aforementioned contaminants. Furthermore, most of these colorimetric methods are based on the formation of coloured lakes, which are sensitive to experimental conditions and are difficult to reproduce. Aluminium does react with 8-quinolinol, however, to form an extremely stable chelate which is extractable into chloroform.[12]

Of the reported methods for the determination of aluminium in thorium by utilization of 8-quinolinol, no particular difficulties are encountered as long as certain contaminants are absent. For example, in the method of Margerum, Sprain, and Banks,[9] aluminium quinolinate is extracted by chloroform from a 6*M* ammonium acetate solution at a pH of 4.7. The extraction under these conditions is effective in the separation of aluminium from thorium and many other metals; however, titanium and relatively larger quantities of iron, which interfere, are not eliminated by such a procedure. In another method, developed by Claasen, Bastings, and Visser,[3] aluminium quinolinate is extracted in the presence of ethylene-diaminetetra-acetic acid (EDTA) which masks most of the interfering elements; however, not only is this procedure time-consuming but it is not applicable if the test portion contains more than 25 mg of thorium.

Since it was desired to determine even sub-microgram quantities of aluminium in thorium, it was believed that a fluorometric method would offer more sensitivity for the detection of such small amounts of this element;[4] however, when the determination of aluminium is made fluorometrically following extraction, the effect of interfering substances is even more pronounced than in the colorimetric methods. In view of the limitation of the existing methods for adaptation to the estimation of such small quantities of aluminium, the problem was to develop a separation scheme whereby large amounts of thorium, as well as the other elements which may be present in thorium oxide, can be removed so effectively that the aluminium can be measured either fluorometrically or colorimetrically.

A separation scheme, which is described in this paper, was developed whereby thorium, iron, zirconium, and copper can be removed from the aluminium by an extraction with a hexone solution of thenoyltrifluoroacetone (TTA) from a 2*M* ammonium acetate medium at a pH of 1.5. Under these conditions, titanium, uranium, molybdenum and vanadium are partially extracted. After this prior separation, the aluminium quinolinate is extracted into chloroform at a pH of 8 in the presence of hydrogen peroxide and nitrilotriacetic acid to mask the interferences of such elements as titanium, vanadium, uranium, and small amounts of thorium. If nickel, zinc, or cadmium are present, a back-extraction can be made of the chloroform extracts with an alkaline cyanide solution to remove these interfering elements. In special cases, when manganese and cobalt are known to be present, an extraction of the diethyldithiocarbamate complexes of these elements is made to separate them from the aluminium. After the removal or masking of all interferences, the aluminium is determined, as the quinolinate, either spectrophotometrically or fluorometrically.

EXPERIMENTAL

Apparatus

Beckman, Model DU, spectrophotometer, with photomultiplier attachment.
Beckman fluorescence accessories.
Beckman, Model H, pH meter.

Reagents

Acetate buffer, pH 8. Dissolve 200 g of ammonium acetate in water. Add 70 ml of concentrated ammonium hydroxide; then dilute the solution to one litre with water.

Alkaline cyanide solution. Dissolve 40 g of ammonium nitrate and 20 g of potassium cyanide in water. Add 10 ml of ammonium hydroxide and dilute the solution to one litre with water.

Ammonium hydroxide, 1 : 1.

Aluminium, standard solution, 100 μg Al/ml. Dissolve 1.7 g of $AlNH_4(SO_4)_2.12H_2O$ in water and dilute to 1 litre. Standardise gravimetrically by the 8-hydroxyquinoline method.[7] Prepare a solution containing 10 μg Al/ml by appropriate dilution of the stock solution.

Nitrilotriacetic acid (NTA), 0.2*M*. Weight 40 g of nitrilotriacetic acid, $(HOCOCH_2)_3N$, into a 600-ml beaker. Add 200 ml of water; then insert the electrodes of a pH meter into the solution. Slowly add a dilute solution of 2*M* sodium hydroxide until the nitrilotriacetic acid (NTA) has dissolved and the pH is 7. Dilute this solution to one litre with water.

8-*Quinolinol*, 2%, in 1*M* acetic acid. Dissolve 20 g of 8-quinolinol in 60 ml of glacial acetic acid. Dilute to one litre with water.

Sodium diethyldithiocarbamate, 2%. Dissolve 2 g of the reagent, $(C_2H_5)_2NCSSNa$, in water. Filter; then dilute to 100 ml.

Thenoyltrifluoroacetone (TTA), 0.5*M*. Dissolve 110 g of TTA in one litre of hexone (4-methyl-2-pentanone).

Sodium sulphate, anhydrous.
Hydrogen peroxide, 3%.
Perchloric acid, 72%.
4-Methyl-2-Pentanone (hexone), reagent grade.
Chloroform, reagent grade.

Extraction with thenoyltrifluoroacetone

Thenoyltrifluoroacetone (TTA), which has been studied as an extractant for many elements,[10] is particularly useful in the separation of thorium, iron, and zirconium. These elements are extractable from solutions at a pH of 2 or lower, whereas aluminium, nickel, and the tervalent rare-earth elements are among the elements which are extractable only from more weakly acidic solutions. From preliminary experiments, it was established that, at a pH of 1.5, zirconium is extracted, while large quantities of thorium (100 mg) are almost completely extracted; however, the extraction of iron proceeds slowly and an extended period of equilibration is necessary. Since the extractability of some elements is noticeably increased if acetate is present in the extraction medium, studies were made of the effect of acetate on the extraction of the interfering elements with a carbon tetrachloride solution of TTA. It was found that, by using an ammonium acetate buffer, the rate at which iron is extracted is increased considerably, and that, by utilizing an extraction medium 2*M* in acetate at a pH of 1.5, iron, thorium, zirconium, and copper are rapidly extracted. Under these same conditions, titanium, uranium, molybdenum, and vanadium are at least partially extracted.

After establishing these experimental conditions, however, it was discovered that, when aluminium is subsequently extracted at a pH of 8 into chloroform as the quinolinate, the results had a tendency to be high when compared to standards which were not subjected to a TTA extraction. This was apparently due to the absorbancy of residual TTA, which was extracted with the aluminium. In order to circumvent this source of error, without resorting to a time-consuming wet-oxidation procedure, tests were made to determine if the interference could be reduced or eliminated by the use of a different organic solvent for the TTA. When carbon tetrachloride, chloroform, or xylene is used as the solvent, interference from residual TTA is encountered; however, when hexone is utilized as the solvent and as a wash solution for the aqueous phase following the extraction with TTA, no extraneous absorbancy is noted. This is probably due to the fact that the distribution ratio of TTA between the organic and aqueous phases is much greater when hexone is used than it is with any of the other solvents. For example, approximately 2% of the TTA is extracted into the aqueous phase fom carbon tetrachloride, but only about 0.2% from hexone.

Use of masking agents to eliminate interfering elements

Although the extraction with TTA in hexone is most effective for the removal of a great many elements, some, of course, are either not extractable at all or only partially so into this medium. In fact, as much as one mg of thorium may be found in the aqueous phase after extraction with TTA. It was necessary, therefore, to seek other means of removing other interfering elements. Since titanium, vanadium, and uranium are only incompletely extracted into TTA under the experimental conditions necessary to remove thorium, iron and zirconium, it was important that some means be provided to prevent their extraction with aluminium into chloroform. Hydrogen peroxide,[5] which has been used to mask titanium, vanadium, and uranium, is, therefore, added to the test portion after the extraction with TTA and before the extraction of aluminium into chloroform from a basic solution.

From experimental data, it was observed that even the smallest amounts of thorium interfere in the extraction of aluminium. It was necessary, therefore, to devise a means of either removing or eliminating any traces of thorium that remain with the aluminium after the extraction with TTA. Ethylenediaminetetra-acetic acid (EDTA) was investigated as a possible complexing or masking agent for thorium; however, the aluminium was incompletely extracted. From additional tests, it was established that nitrilotriacetic acid (NTA) is effective in preventing the extraction of up to 2 mg of thorium as the quinolinate, and that, furthermore, it has no effect on the extraction of aluminium.

Cyanide, which has been used previously to mask certain elements,[6] was utilized in this procedure to mask the interference of nickel, copper, zinc, and cadmium by washing the chloroform extract which contained the aluminium quinolinate with 100 ml of an alkaline solution of cyanide.

By the use of a combination of these masking agents, therefore, it is possible to separate aluminium effectively from many substances which interfere in the subsequent colorimetric or fluorometric measurements.

TABLE I. EFFECT OF VARIOUS ELEMENTS ON THE SEPARATION AND DETERMINATION OF ALUMINIUM

(Other ions present: Thorium, *mg*, 100 Iron, *mg*, 0.5 Titanium, *mg*, 0.5)

Interference		Aluminium, *μg*		
Ion	Amount, *μg*	Added	Found	Difference
Method: Spectrophotometry				
Cu^{+2}, Zn^{+2}	1000	50.0	51.5	1.5
U^{+6}	1000	50.0	50.3	0.3
Zr^{+4}	1000	50.0	52.5	2.5
Ce^{+3}	1000	50.0	52.3	2.3
V^{+5}	1000	50.0	50.3	0.3
Sn^{+4}	1000	50.0	74.7	24.7
Cd^{+2}	1000	50.0	49.7	−0.3
Ni^{+2}	1000	100	97.0	−0.3
Mo^{+6}	1000	100	101	1
W^{+6}	1000	100	102	2
Cr^{+3}	1000	100	130	30
Mn^{+2}	100	100	177	77
Co^{+2}	100	100	118	18
Method: Fluorometry				
Ni^{+2}	30	0.5	0.47	0.03
Cu^{+2}	30	0.5	0.43	0.07
Zn^{+2}	30	0.5	0.45	0.05
Mn^{+2}, Co^{+2}	5	1.0	1.06	0.06
Mn^{+2}, Co^{+2}	5	2.0	2.06	0.06
Mn^{+2}, Co^{+2}	5	6.0	6.02	0.02
Mn^{+2}, Co^{+2}	5	8.0	7.71	−0.29

The results from the spectrophotometric and fluorometric estimation of aluminium, utilizing a thenoyltrifluoroacetone extraction in conjunction with an 8-quinolinol extraction of the aluminium in the presence of masking agents, are presented in Table I. The test solutions contained, in addition to the ions tabulated, 100 mg of thorium and 0.5 mg each of iron^{III} and titanium^{IV}.

The residual thorium, up to 2 mg, is masked by the addition of nitrilotriacetic acid to the solutions before the aluminium-quinolinate extraction. The titanium, vanadium and uranium, which are not removed by the TTA extraction, are masked by the addition of hydrogen peroxide to the extraction medium. Of the elements which were not extracted at all by thenoyltrifluoroacetone and interfere in the determination of aluminium, chromium and tin can be volatilized in the initial decomposition of the sample by adding a few drops of hydrochloric acid to the fuming perchloric acid solution. Nickel, cadmium and zinc are removed by washing the chloroform extracts containing their quinolinates with the alkaline cyanide solution. Only manganese and cobalt interfere seriously if present in quantities greater than 50 ppm in the original sample.

The data from the fluorometric determination of small quantities of aluminium, utilizing the same separation scheme, are likewise tabulated in Table I. In estimating small quantities of aluminium by this method however, extreme care must be taken to avoid the pick-up of aluminium in the solutions and reagents. For this reason, it is recommended that all glassware be rinsed with dilute nitric acid and water before use and that the reagents be stored in polyethylene containers.

Removal of manganese and cobalt with sodium diethyldithiocarbamate

In considering special cases where manganese and cobalt were present in the samples in amounts exceeding the tolerance limits, the use of sodium diethyldithiocarbamate, a reagent which forms extractable complexes with these elements[2,8] but not with aluminium, was tested. These tests were made by extracting, at various pH values, manganese and cobalt from a solution, which contained 2 ml of a 2% solution of sodium diethyldithiocarbamate, with two 20-ml portions of chloroform. The results of these tests are presented graphically in Figure 1. Since manganese is extracted with diethyldithiocarbamate only at a pH above 6, a pH of 9 was selected for use in other experiments. Although small losses of aluminium do occur in extractions at the higher pH, as noted in Figure 1, a calibration curve can, nevertheless, be prepared, as depicted in Figure 2. Results of this extraction procedure, at a pH of 9, are shown in Table II.

TABLE II. DETERMINATION OF ALUMINIUM AFTER REMOVAL OF INTERFERENCES BY ADDITION OF SODIUM DIETHYLDITHIOCARBAMATE AND EXTRACTION WITH CHLOROFORM AT pH 9 (Aluminium Present, 100 μg)

Ion	Amount, *mg*	Aluminium recovered, μg	Difference
Mn^{+2}	1	98	2
Ni^{+2}	1	101	1
Sn^{+4}	1	99	1
Zn^{+4}	1	103	3
Co^{+2}	0.2	102	2
Cu^{+2}	0.2	103	3
Cd^{+2}	0.2	103	3
Cr^{+3}	0.2	49	51

In the extraction with diethyldithiocarbamate, in addition to manganese and cobalt, nickel, zinc, and cadmium are also extracted as their carbamates. It is not necessary, therefore, to use the alkaline cyanide method to eliminate these elements. In the presence of chromium^{III} and small amounts of thorium which remain after the extraction with TTA, the recovery of aluminium is low when an extraction with diethyldithiocarbamate is made. Chromium can be removed by volatilization. Although the loss of aluminium is dependent on the amount of thorium present, a calibration curve can be prepared if the amount of thorium is maintained at a fixed level of approximately 1 milligram.

In order to eliminate the necessity of controlling the amount at approximately 1 mg, an alternate scheme of separation was developed for samples which contain manganese and cobalt, but no titanium. In this alternate method, following the TTA extraction, an extraction with diethyldithiocarbamate was carried out at a pH of 1.5. At this pH, aluminium is not lost and the thorium which remains in the aqueous phase after the initial TTA extraction does not affect the recovery of aluminium. The extraction of aluminium was subsequently made at a pH of 5 in the presence of 1*M* acetate. The high concentration of acetate serves as a masking agent for thorium, while manganese does not react with 8-quinolinol at a pH of 5. Results from this alternative procedure are given in Table III.

Primary interferences in this procedure are tin, which can be removed by volatilization, and titanium, which must be absent. Manganese, cobalt, and chromium do not interfere. A back-extraction with an alkaline cyanide solution is unnecessary, since those substances that ordinarily are removed by the cyanide are extractable as the carbamates at a pH of 1.5.

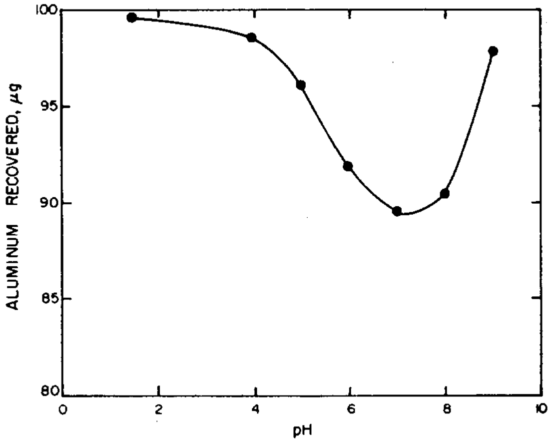

FIG. 1. Recovery of aluminium as the quinolate after removal of interferences by extraction with sodium diethyldithiocarbamate and chloroform at different pH values aluminium, *μg*, 100

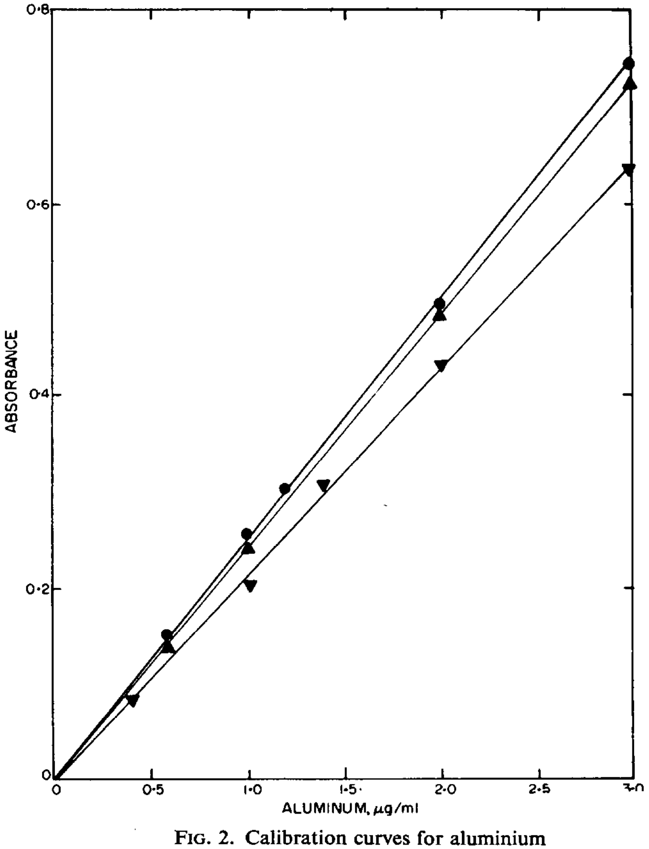

FIG. 2. Calibration curves for aluminium

● Extraction of aluminium with 8-quinolinol at pH 5 or pH 8.

▲ After extractions with sodium diethyldithiocarbamate at pH 9, followed by 8-quinolinol extraction at pH 9.

▼ After extractions with sodium diethyldithiocarbamate at pH 9 in the presence of 1 mg of thorium, followed by 8-quinolinol extraction at pH 9.

RECOMMENDED PROCEDURE

Preparation of calibration curves

Spectrophotometric measurement. Transfer 3-, 10-, and 15-ml portions of a standard solution of aluminium (10 μg/ml) to a 150-ml beaker; then dilute the solution to approximately 75 ml. Add 5 ml of 0.2*M* nitrilotriacetic acid, 2 ml of a 3% solution of hydrogen peroxide, 2 ml of the acetate buffer solution, and 2 ml of a 2% solution of 8-quinolinol. Adjust the pH of each sample to 8 with 1 : 1 ammonium hydroxide. Transfer the solutions to 250-ml separatory funnels; then extract each standard twice with 20-ml portions of chloroform. Each extraction requires about two minutes. Combine the two organic phases in 50-ml flasks which contain about one gram of anhydrous sodium sulphate; then dilute to volume with chloroform. Measure the absorbancy of each sample at a wave-length of 390 mμ against a reagent blank, using 1-cm cells.

TABLE III. DETERMINATION OF ALUMINIUM AFTER REMOVAL OF INTERFERENCES BY A CHLOROFORM EXTRACTION AFTER ADDITION OF SODIUM DIETHYLDITHIOCARBAMATE FOLLOWED BY EXTRACTION WITH 8-QUINOLINOL AT pH OF 5

(Aluminium, 100 μg)

Interferences		Aluminium recovered μg	Difference
Ion	Amount, *mg*		
Mn^{+2}	1	99	1
Co^{+2}	1	100	0
U^{+6}	1	103	3
Mo^{+6}	1	105	5
Cu^{+2}	1	102	2
Cd^{+2}	1	99	1
Zn^{+2}	1	102	2
W^{+6}	1	102	2
Ni^{+2}	1	99	1
Sn^{+4}	1	117	17
Ti^{+4}	1	183	83
Cr^{+6}	0.5	104	4
Cr^{+3}	0.5	106	6

Fluorometric measurement. Transfer test portions of the standard solution of aluminium which contain from 1 to 10 μg of aluminium into 150-ml beakers. Proceed with the method as described under "Spectrophotometric Measurement." After the samples are diluted to the final volume of 50-ml, measure the fluorescent intensity *versus* a reagent blank by means of a Beckman, Model DU, spectrophotometer that is equipped with a Beckman fluorescent attachment. For these measurements, follow the procedure outlined in the manual supplied with the instrument.[1]

Determination of aluminium in thorium oxide

Weigh a 0.1-g sample (5 to 1500 ppm of aluminium) of thorium oxide into a 50-ml beaker. Dissolve the sample by boiling it gently in 20 ml of 1 : 1 nitric acid that contains a few drops of hydrofluoric acid. When dissolution is complete, add 3 ml of perchloric acid and evaporate to fumes. Cool the sample to room temperature; then add 5 ml of water and 8 ml of 50% ammonium acetate, and adjust the pH to 1.5 with perchloric acid. Transfer the sample to an extraction cup and adjust the volume of the solution to 25 ml with water. Add 10 ml of 0.5*M* TTA dissolved in hexone; then stir the mixture mechanically for five minutes. Drain the aqueous phase into another extraction cup and repeat the extraction with an additional 10-ml portion of TTA in hexone. Drain the aqueous phase into another extraction cup; then wash the solution by stirring it mechanically with 10 ml of hexone for 3 minutes. Transfer the aqueous phase to a 150-ml beaker, and proceed as directed in the section "Calibration Curve." Measure either the absorbancy or fluorescent intensity as dictated by the concentration of aluminium in the sample.

If iron, zirconium, and copper are present in the thorium oxide, they are also removed by the extraction with TTA. Titanium, uranium, and vanadium, if present, are partially extracted; the hydrogen peroxide, however, is used to mask the interference of these elements.

In the presence of nickel, zinc, and cadmium

If the sample contains nickel, zinc, or cadmium, follow the procedure outlined above until the aluminium has been extracted as the quinolinate; then transfer the chloroform extracts to a 250-ml separatory funnel which contains 100 ml of an alkaline cyanide solution. Shake the solution for about 2 minutes; then drain the organic phase into a 50-ml volumetric flask and proceed as directed under the section "Calibration Curve."

In the presence of manganese and cobalt

Titanium present. If manganese and cobalt in addition to titanium are present, after the extraction with TTA in hexone, add two ml of a 2% solution of diethyldithiocarbamate to the aqueous portion of the extract; then adjust the pH to 9. Add 20 ml of chloroform and extract the solution for two minutes. Transfer the aqueous phase to a 150-ml beaker, and proceed as directed in the section "Calibration Curve."

Titanium absent. When the sample contains manganese and cobalt but no titanium, a slightly different procedure is followed. After the extraction of thorium with TTA, transfer the aqueous phase to a separatory funnel, add 2 ml of a 2% solution of diethyldithiocarbamate; then adjust the pH to 1.5. Extract the solution with two, 20 ml portions of chloroform. Transfer the aqueous phase to a 150-ml beaker, and then dilute it to approximately 75 ml. Add 5 ml of $0.2M$ nitrilotriacetic acid, and sufficient acetate buffer to make the solution $1M$ with respect to acetate. Adjust the pH to 5; then transfer the sample to a separatory funnel, and extract the aluminium quinolinate in the usual manner.

DISCUSSION

Although the method described in this paper has been applied only to the determination of aluminium in thorium oxide, it is probable that other types of samples can be analyzed for aluminium by the same procedure. This would include, particularly, those samples that contain large amounts of elements which are easily extractable with hexone solutions of thenoyltrifluoroacetone, such as zirconium or others, such as molybdenum, which are not extracted by 8-quinolinol at a pH of 8. Approximately one hour is required to complete the analysis. The coefficient of variation for the spectrophotometric method is about 3% while for the fluorometric method it is about 5%.

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Zusammenfassung—Es wird eine Methode zur Trennung und Bestimmung von 0,5 bis 150 μg von Aluminium in Thoroxyd angegeben, die Korrosionprodukte von Stahl und anderen Unreinigkeiten enthält. Das Aluminium wird von Thorium, Eisen, Zirkon und einigen anderen Elementen durch Extrahierung mit einer Hexonlösung von Thenoyltrifluoroaceton (TTA) getrennt. Aluminium wird dann mit 8-Chinolinol und Chloroform in Anwesenheit von Wasserstoff-hyperoxyd, Natrium-cyanid und Nitrilotriessigsäure extrahiert, welche die störenden Ionen maskieren. Man kann das Aluminium entweder fluorometrische oder spektralphotometrische messen. Wenn das Thoroxyd auch Mangan und Kobalt enthält, ist eine Doppel-Extrahierung mit TTA und Natrium-diäthyl-dithio-carbamat notwendig, bevor man das Aluminium als Chinolinat erfolgreich bestimmen kann.

Résumé—On présente une méthode de séparation et détermination ultérieure de 0,5 à 150 μg d'aluminium dans de l'oxyde de thorium contenant des produits de corrosion d'acier et d'autres impuretés. L'aluminium est séparé du thorium, du fer, du zirconium et de quelques autres éléments par extraction de ces éléments avec une solution de thenoyltrifluoroacétone (TTA) dans l'hexone. L'aluminium est alors extrait avec de l'hydroxy-8-quinaldine et du chloroforme en présence d'eau oxygénée, de cyanure de sodium et d'acide nitrilo-acétique qui masquent les ions gênants qui ne sont pas séparés par l'extraction au TTA. Etant donnée l'efficacité des séparations pour éliminer les interférences, l'aluminium peut être dosé soit par fluorométrie, soit par spectrophotométrie, suivant la quantité à déterminer. Quand l'oxyde de thorium contient aussi du manganèse et du cobalt, une double extraction, utilisant du TTA et du diethyldithiocarbamate de sodium est nécessaire pour séparer les ions gênants avant que l'aluminium ne puisse être déterminé avec succès à l'état d'hydroxy-8-quinaldinate.

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ANALYTICAL APPLICATIONS OF XYLENOL ORANGE—I

DETERMINATION OF TRACES OF ZIRCONIUM

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Summary—The red colour of the zirconium-Xylenol Orange complex has been utilised in the development of a very sensitive and highly selective method for the determination of traces of zirconium. The molar absorptivity of this complex in 0.2*N* sulphuric acid medium is 33,840 at 535 mμ. Amounts of zirconium from 5 to 62 μg per 25 ml follow Beer's law. Iron^{III}, cerium, and bismuth interfere but can be masked by employing ascorbic acid, chloride, or other masking agents. The interference of large amounts of molybdenum, niobium and tin^{II} has been discussed.

XYLENOL Orange, [3:3′-bis-N:N-di(carboxymethyl)-aminomethyl]-*o*-cresolsulphonphthalein, was first introduced by Körbl and Přibil as a metal indicator in the EDTA titration, and the lower pH limit with respect to its cation reactions was also reported[1]. Other papers in the literature dealing with Xylenol Orange also limit its use as an indicator in the ethylenediaminetetra-acetic acid (EDTA) titration. This paper reports the use of this dye as a sensitive and selective colorimetric reagent for zirconium. It can also be used for determining hafnium since the dye reacts similarly with hafnium. Other analytical applications of this dye will be reported in the future.

The methods of determining micro amounts of zirconium have been reviewed by Young *et al.*[2]. They stated that pyrocatechol violet was superior to other reagents for zirconium such as alizarinesulphonic acid, *p*-dimethylaminoazophenylarsonic acid, quercetin, 2-(2-hydroxy-3:6-disulpho-1-naphthylazo)-benzenarsonic acid (Thoron), 2-(*p*-sulphophenylazo)-1:8-dihydroxy-3:5-naphthalenedisulphonic acid (SPADNS), and chloranilic acid, due to the fact that either they are less sensitive for zirconium or they are subject to interferences from sulphate, iron, thorium, etc. The present work has shown that Xylenol Orange is more sensitive, more selective, and can tolerate higher acidity (up to 1*N* perchloric acid) than pyrocatechol violet and other analytical reagents used for zirconium. But Xylenol Orange tolerates less amounts of sulphate ions than pyrocatechol violet. Perchloric acid may be advantageously used for the preparation of samples and for the mercury cathode separation when Xylenol Orange is used for determining zirconium.

APPARATUS AND REAGENTS

The absorption spectra of Xylenol Orange and its zirconium complex were measured with a Cary Spectrophotometer, Model 14, with 1-cm quartz cells. Other absorbance measurements were made with the Spectronic 20 Colorimeter. A Beckman Model G pH meter was used. The Dyna Cath was used for the mercury cathode separation.

Xylenol orange: 0·05% aqueous solution of its sodium salts. Xylenol Orange in acid form is slightly soluble in water but soluble in alcohol. Its sodium salt is not so soluble in alcohol but very soluble in water and hydroscopic.

Standard zirconium solution: Appropriate standard solutions were prepared from a stock zirconium tetrachloride solution in 0·2*N* sulphuric acid or 0.8*N* perchloric acid. The stock solution was standarized by the EDTA titration.[1] Standard stock zirconium solution may also be prepared from pure zirconium metal in 4*M* sulphuric acid.[2]

EXPERIMENTAL

Calibration curve

Pipette from 5 to 60 μg of zirconium into a 25-ml volumetric flask. Add 2 ml of 2.5*N* sulphuric acid or 4 ml of 5*N* perchloric acid and 2 ml of 0.05% Xylenol Orange solution. Dilute to the mark with water and mix. Measure the absorbance at 535 mμ using the reagent blank. Beer's law is followed.

Absorption spectra

Xylenol Orange is an acid-base indicator, changing colour from yellow to purple starting at pH 6.0. Solutions of Xylenol Orange are light pink in 1 : 1 or concentrated sulphuric acid. The yellow solution of the dye shows a maximum absorption at 437 mμ and its red zirconium complex at 535 mμ (see Fig. 1).

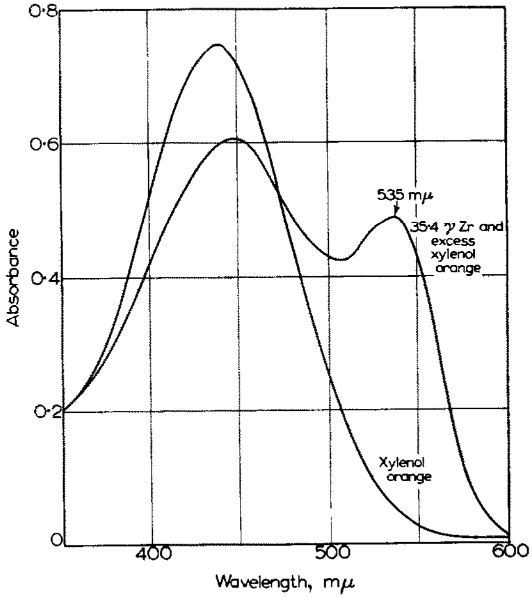

FIG. 1

Effect of acid

Figure 2 shows that the optimum sulphuric acid concentration for the colour formation of zirconium-Xylenol Orange complex is 0.15 to 0.25*N*, therefore a concentration of 0.2*N* is recommended. The decrease in colour intensity at an acidity higher than 0.25*N* is due to the fact that high acidity and high concentration of sulphate tend to break the zirconium complex. The decrease

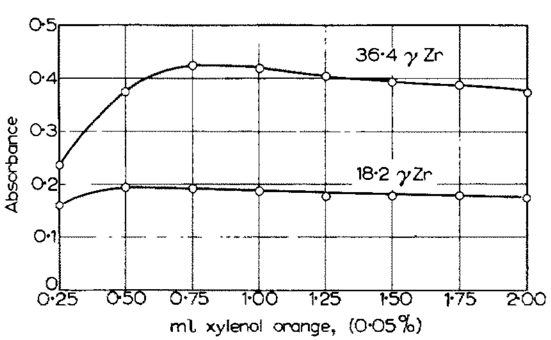

FIG. 2

in colour intensity at an acidity lower than 0.15*N* is probably caused by the hydrolysis of zirconium. In the case of high concentration of sulphate acid, the decrease is proportional to the amount of zirconium present. It shows approximately the same percentage of decrease based on the amount of zirconium present. The effect of concentrations of hydrochloric acid and perchloric acid was also studied. Both hydrochloric and perchloric acids at 0.8*N* give a maximum colour development (Figure 3). In perchloric acid medium the solution should be left standing for 2 hours or longer in order to obtain maximum colour development.

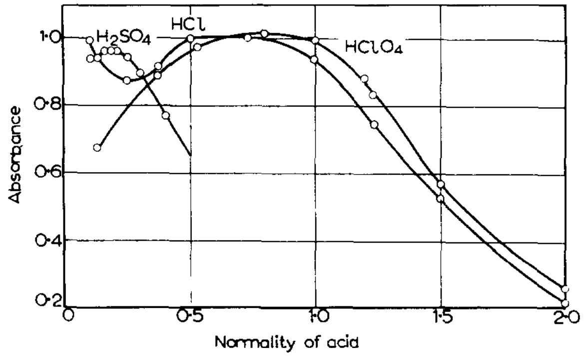

FIG. 3

Effect of sulphate

Sulphate is often a major interfering anion for most colorimetric methods for zirconium. It is reported[2] that the absorbance of the zirconium-pyrocatechol violet complex is enhanced in the presence of high concentrations of sulphate at pH 5.1. However, the present investigation illustrates that the absorbance of the zirconium-Xylenol Orange complex is slightly decreased in the presence of high concentrations of sulphate (above 2 mmoles in 25 ml) as shown in Table I. This is probably caused by the formation of an appreciable amount of zirconium sulphate complex in a rather acid medium.

TABLE I.—EFFECT OF SULPHATE ON ABSORBANCE OF ZIRCONIUM-XYLENOL ORANGE COMPLEX

(Zr taken = 35.4 μg per 25 ml)

K_2SO_4 Added *mmole*	Absorbance, 535 mμ
0	0.505
1.0	0.505
2.0	0.500
2.5	0.480
5.0	0.450
7.5	0.420
10.0	0.410
20.0	0.390

Effect of amount of Xylenol orange

It was found that 1.5 ml of 0.05% Xylenol Orange solution was sufficient for the amounts of zirconium studied. Too much Xylenol Orange tends to give a slightly lower absorbance as shown in Figure 3. It must be mentioned that the amount of Xylenol Orange not only depends on the amount of zirconium to be determined but also on the purity of the dye.

Sensitivity

The molar absorptivity of the zirconium-Xylenol Orange complex is found to be approximately 33,840 at 535 mμ and slightly higher than that of the zirconium-pyrocatechol violet complex which is reported[2] to be 32,600.

Specificity

A qualitative test was conducted as follows: To one drop of $0.01M$ metal solution to be tested, two drops of $0.25N$ sulphuric acid and 1 drop of 0.05% Xylenol Orange solution were added. For studying the effect of the masking agents, the solutions of masking agent were added before addition of the Xylenol Orange solution.

Under the conditions tested, the following elements do not give a positive test (red colour): Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Al, Sc, Y, La, Ti, V, Ta, Cr, Mo, W, Mn, Re, Fe^{II}, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Ce, Si, Ge, Sn^{IV}, Pb, P, As, Sb, S, Se, Te, F, Cl, Br, I, Ce^{III}, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, and U. Cerium^{IV} as well as other oxidising agents bleach the dye. Zirconium, hafnium and bismuth give a deep red colour with Xylenol Orange. Iron^{III} gives a violet colour. Tin^{II} and large amounts of niobium give a light pink colour which turns yellow in more acid medium ($0.5N$) in which both zirconium and bismuth still give a red coloration. Molybdenum^{VI} gives a brownish-yellow colour. Hydrogen peroxide masks molybdenum, niobium, and zirconium; but it only partially masks hafnium resulting in a brownish-red colour instead of red. It would be interesting to employ such masking action to differentiate hafnium from zirconium.

The above simple test has already demonstrated the highly selective colour reactions for zirconium (and hafnium), iron, and bismuth. Table II illustrates that the test can be made more specific for these metals if suitable masking agents are used. For a test for zirconium (and hafnium), in the presence of bismuth and iron, chloride and ascorbic acid should be added. If tin^{II} or niobium is present, zirconium may be tested at an acidity of 0.3 to $0.5N$ sulphuric acid, which only slightly decreases the sensitivity for zirconium. Since the zirconium complex shows a slightly higher sensitivity and tolerates higher acidity in perchloric acid medium, it seems that the development

TABLE II.—EFFECT OF MASKING AGENT ON COLOUR REACTION OF METALS WITH XYLENOL ORANGE ($0{\cdot}2N$ H_2SO_4 medium)

Masking Agent	Amount	Not Masked	Masked
Chloride	0.2 g NaCl	Fe^{III}, Zr, Hf, Sn^{II}, Nb	Bi
Iodide	5 mg KI	Zr, Hf, Sn^{II}, Nb	Bi, Fe^{III}
Fluoride	2 drops 0.1% KF	Bi, Fe^{III}	Zr, Hf, Sn^{II} Nb
Thiourea	1 drop 5%	Zr, Hf, Sn^{II}, Nb	Fe^{III}, Bi
Thiosulphate	1 drop 10% Na salt	Zr, Hf, Sn^{II}, Nb	Fe^{III}, Bi
Citrate	2 drops 5% Na salt	Bi, Fe^{III}, Nb	Zr, Hf, Sn^{II}
Orthosphophate	1 drop $1M$ H_3PO_4	none	Bi, Fe^{III} (partially) Sn^{II}, Zr, Hf, Nb (completely)
Ascorbic acid	10 mg	Zr, Hf, Bi, Sn^{II}	Fe^{III}, Mo
EDTA	2 drops $0.1M$	Nb	Fe^{III}, Bi, Zr, Hf
Hydrogen peroxide	2 drops 30%	Fe^{III}, Bi	Mo, Nb, Zr, Hf (partially)

of the colour in a perchloric acid medium may offer more advantages; the presence of tin^{II} and molybdenum does not give any red coloration with Xylenol Orange in $0.8N$ perchloric acid medium.

Anions

Chloride, bromide, iodide, nitrate, sulphate, perchlorate, (except large amounts, see Table II and Figure 2), thiourea and acetate do not interfere. Fluoride, EDTA, NTA, citrate, tartrate, oxalate, thiosulphate (turbidity caused by deposition of sulphur), and phosphate interfere.

Determination

The above general procedure was applied to the determination of zirconium in the presence of foreign cations. As illustrated in Table III, most cations do not interfere except niobium, molybdenum and hafnium. Bismuth and $iron^{III}$ can be masked by chloride and ascorbic acid; the interference of tin^{II}, niobium, and molybdenum may be prevented by using lower pH, 0.3 to $0.5N$ sulphuric acid. Small amounts of niobium and molybdenum do not interfere. Although cobalt, copper, nickel, $chromium^{III}$, etc. do not interfere, their intensely coloured solutions may disturb the absorbance measurement. In such cases, a mercury-cathode separation may be used.

TABLE III.— DETERMINATION OF ZIRCONIUM IN PRESENCE OF FOREIGN METALS

(Zirconium taken = 35.4 μg in 25 ml.)

Metal Added	Amount *mmole*	Zirconium found, μg	Metal Added	Amount *mmole*	Zirconium Found, μg
None	—	35·4	*Fe^{III}	10^{-2}	35.4
			Co^{II}	10^{-2}	35.3
Be	10^{-2}	35.4	Ni	10^{-2}	35.5
Al	10^{-2}	35.4	Cu	10^{-2}	35.5
Sc	10^{-2}	35.4	Zn	10^{-2}	35.6
Y	10^{-2}	35.4	Cd	10^{-2}	35.5
La	10^{-2}	35.4	Hg	10^{-2}	35.5
Ti^{IV}	10^{-2}	35.4	Ga	10^{-2}	35.5
V^{V}	10^{-2}	35.0	In	10^{-2}	35.5
Nb	10^{-3}	60.0	Sn^{IV}	10^{-2}	36.0
Nb	5×10^{-4}	38.0	Sn^{II}	10^{-2}	44.5
Ta	10^{-2}	35.4	Pb^{II}	10^{-2}	35.4
Cr^{III}	10^{-2}	36.0	†Bi	10^{-2}	35.4
Mo^{VI}	10^{-2}	41.0	Ce^{IV}	10^{-2}	35.5
Mo^{VI}	10^{-3}	35.4	Th	10^{-2}	35.4
W	10^{-2}	34.0	UO_2^{II}	10^{-2}	35.5
W	10^{-3}	35.0			
Mn	10^{-2}	35.4			

* 0.3 gram of ascorbic acid added.

† One gram of sodium chloride added.

Zusammenfassung—Die rote Farbe des Zirkon-Xylenol-Orange-Komplexes wird in der Entwicklung einer sehr empfindlichen und hoch-selektiven Methode zur Bestimmung der Zirkonen-Spuren gebraucht. Die Mol-Absorbtivität dieses Komplexes in $0,2N$ Schwefelsäure ist 33 840 bei 535 mμ. Die Mengen des Zirkons von 5 bis 63 μg pro 25 ml folgen dem Beer'schen Gesetz. Eisen-III, Cer und Wismuth stören, dies kann man jedoch durch den Gebrauch von Ascorbinsäure, Chlorid oder von anderen Mitteln maskieren. Die Interferenz der grossen Mengen von Molybdän, Niob und Zinn-II wird erörtert.

Résumé—On a utilisé la coloration rouge du complexe zirconium-orange de xylénol pour mettre au point une méthode très sensible et de haute sélectivité permettant le dosage de traces de zirconium. L'absorptivité molaire de ce complexe en milieu acide sulfurique 0,2*N* est 33 840 à 535 mμ. Les concentrations de zirconium de 5 à 62 μg par 25 ml suivent la loi de Beer. Le fer-III, le cérium et le bismuth gênent mais peuvent être masqués au moyen d'acide ascorbique, d'un chlorure ou d'autres réactifs de masquage. On discute les perturbations dues à la présence de fortes quantités de molybdène, de niobium et d'étain-II.

Acknowledgment—The author is grateful to Dr. R. Přibil and CHEMAPOL for supplying the sample of Xylenol Orange used in this investigation, and to C. Spicer and A. Janus for aid in obtaining some of the results reported.

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UNTERSUCHUNGEN ZUR EXTRAKTIVEN TRENNUNG VON GALLIUM UND INDIUM MIT VERSCHIEDENEN LÖSUNGSMITTELN

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Zusammenfassung—Es wurde der Einfluss des organischen Lösungsmittels bei der Indium-Galliumtrennung aus jodidhaltigen wässrigen Lösungen untersucht. Die bekannte Extraktion des Indiums mit Äther kann mit höheren Ketonen erheblich verbessert werden. Als besonders wirkungsvoll erweist sich die Extraktion mit Cyclohexanon. Schon bei sehr geringen Jodidkonzentrationen und geringer Acidität ist der Trennfaktor grösser als 10^4. Nach demselben Verfahren können die Erdalkalien, Aluminium und Eisen von Indium durch eine Ausschüttelung getrennt werden. Das Indium wird mit Cyclohexanon als Tetrajodo-indat $[InJ_4]^-$ extrahiert.

VOR einiger Zeit berichteten wir über die Abtrennung des Indiums von Gallium durch Extraktion mit Cyclohexanon aus jodidhaltigen wässrigen Lösungen.[1] Verteilungssysteme, die als wesentlichen Bestandteil Jodide enthalten, wurden im Gegensatz zu chlorid-, bromid- und thiocyanathaltigen Systemen bisher nur wenig untersucht.[2,3]. Die qualitative Prüfung des Verteilungsverhaltens verschiedener Elemente zwischen jodidhaltigen wässrigen Lösungen und geeigneten organischen Lösungsmitteln zeigt aber, dass in solchen Systemen gerade diejenigen Metallionen bevorzugt extrahiert werden, die sich aus salzsauren bzw. chloridhaltigen Lösungen nicht, aus bromidhaltigen Lösungen nur teilweise ausschütteln lassen, so etwa Silber, Blei, Cadmium.[4,5] In vielen Fällen beobachtet man eine Umkehrung des Verteilungsverhaltens von

TABELLE I. ABHÄNGIGKEIT DER VERTEILUNGSKOEFFIZIENTEN K_{In} UND K_{Ga} VON DER NATUR DES VERTEILUNGS-SYSTEMS

Verteilungssystem	K_{In}	K_{Ga}	$K_{\mathrm{In}}/K_{\mathrm{Ga}}$
wässrige 7 m Lithiumchloridlösung/Isobutylmethylketon	$\sim 1{,}5^{(a)}$	$>10^{3(a)}$	$\leqq 1{,}5 \cdot 10^{-3}$
wässrige 1 m Kaliumjodidlösung/Isobutylmethylketon	$>10^{2(a)}$	$<10^{-2(a)}$	$\geqq 10^4$
0,25 m Kaliumbromidlösung in 0,1 n H_2SO_4/Cyclohexanon	$\sim 5^{(a)}$	$<10^{-2(b)}$	$>5 \cdot 10^2$
0,25 m Kaliumjodidlösung in 0,1 n H_2SO_4/Cyclohexanon	$>10^{2(a)}$	$<10^{-2(b)}$	$\geqq 10^4$

Phasenverhältnis: V_0/V_w = 50 ml/50 ml
(a) 100 mg Me vorgelegt als $Me_2(SO_4)_3$
(b) 10 mg Me vorgelegt als $Me_2(SO_4)_3$

Metallionen, wenn man von chloridhaltigen zu jodidhaltigen Verteilungssystemen übergeht. In der vorstehenden Tabelle wird dies am Beispiel der Verteilungskoeffizienten K_{In} und K_{Ga} von Gallium und Indium veranschaulicht.

Die Analyse der organischen und der wässrigen Lösungsmittelphasen und die Überprüfung der Verteilungsvorgänge mit Hilfe des JOB'schen Verfahrens der kontinuierlichen Variationen haben ergeben, dass das Gallium als Tetrachlorogallat-Ion—$[\mathrm{GaCl}_4]^-$–, das Indium als Tetrajodoindat-Ion—$[\mathrm{InJ}_4]^{-6}$ extrahiert wird. Diese Befunde enthalten keine Aussage über die mögliche koordinative Bindung von Lösungsmittelmolekeln an die extrahierten Komplexionen. Davon abgesehen liegen in beiden Fällen in der organischen Phase Ionen vom gleichen Bautypus vor. In welcher Weise die Extrahierbarkeit dieser Ionen vom Verhältnis der Radien, der Elektronegativitäten und Polarisierbarkeiten von Zentralatom und Liganden abhängen, ist noch nicht zu übersehen.

Es ist bemerkenswert, dass hohe Verteilungskoeffizienten in den jodidhaltigen Verteilungssystemen schon bei sehr viel geringeren Konzentrationen des komplexbildenden Halogenidions erreicht werden als bei den entsprechenden bromid- und chlorid-haltigen Verteilungssystemen (Abb. 1), ausserdem ist die Extrahierbarkeit viel weniger von der Natur des Gegenkations (H^+, Li^+, Na^+, K^+ usw.) abhängig als bei den chloridhaltigen Systemen.

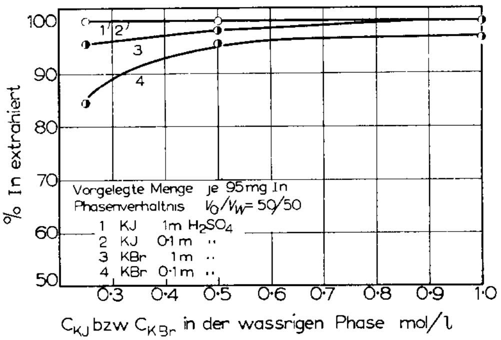

ABB. 1. Extrahierbarkeit von Indium mit Cyclohexanon aus wässrigen Kaliumbromid- und Kaliumjodidlösungen.

Damit sind wesentliche Voraussetzungen für die Anwendung jodidhaltiger Verteilungssysteme zu analytisch und präparativ brauchbaren Trennungen gegeben. Die Wirksamkeit solcher Verteilungssysteme und der mit ihnen zu erzielende Trennfaktor werden indessen nicht nur von der Natur der komplexbildenden Liganden beeinflusst; sie hängen vielmehr auch in starkem Masse von der Acidität des Systems und von dem jeweils verwendeten Lösungsmittel ab. Ganz allgemein sind zu Extraktionen von der hier betrachteten Art Lösungsmittel geeignet, die die Gruppierungen $\underset{\underset{\mathrm{O}}{\|}}{-\mathrm{C}-}$ (Carbonsäureester, Ketone, Kohlensäureglykolester), $\overset{|}{\underset{\underset{\mathrm{O}}{\|}}{-\mathrm{P}-}}$ (Phosphorsäureester, Phosphorigsäureester, Phosphinoxyde) oder die Äthergruppe enthalten.

Wir haben deshalb versucht, am Beispiel der Trennung von Gallium und Indium den Einfluss verschiedener Lösungsmittel, nämlich Diäthyläther, Methylisobutylketon (2-Methylpentanon-4) und Cyclohexanon auf die Extrahierbarkeit der beiden Elemente zu verfolgen und so die optimalen Bedingungen für die Trennung aufzufinden.

EXPERIMENTELLES

Die Verteilungsuntersuchungen wurden in zylindrischen, graduierten Schüttelgefässen von 150 ml Inhalt bei Raumtemperatur vorgenommen. Die Phasen wurden jeweils 2 min lang kräftig geschüttelt; Vorversuche hatten ergeben, dass das Verteilungsgleichgewicht sich innerhalb von 30–40 sec vollständig einstellt.

Sämtliche Lösungsmittel wurden vor der Verwendung durch Destillation gereinigt. Im übrigen wurden handelsübliche, analysenreine Chemikalien verwendet (Schwefelsäure p.a., Merck, Kaliumjodid p.a. Merck, Kaliumbromid p.a. Merck). Die Lösungen von Gallium(III)-sulfat und Indium(III)-sulfat wurden durch Lösen und Abrauchen der reinen Metalle mit Schwefelsäure hergestellt. Die Gehalte der Lösungen an Gallium bzw. Indium wurden durch mehrfache gravimetrische Bestimmung als Galliumoxinat bzw. als Indium(III)-oxyd ermittelt.

Nach vollständigem Absitzen der wässrigen Phase im Schüttelgefäss wurde diese abgetrennt und ihr Metallgehalt gravimetrisch bestimmt. Die organische Phase wurde quantitativ in ein Becherglas überführt und mit Wasser unterschichtet; das organische Lösungsmittel wurde auf dem Sandbad abgedampft und der Metallgehalt der verbleibenden wässrigen Lösung gravimetrisch ermittelt.

DISKUSSION

Die Ergebnisse der Verteilungsuntersuchungen sind in den Abbildungen 2, 3 und 4 zusammengestellt.

In dem gesamten, von uns untersuchten Bereich der Zusammensetzung der wässrigen Ausgangslösung wird das Gallium nicht extrahiert (Kurve 4 in Abb. 2 und Abb. 4). Die Extrahierbarkeit des Indiums variiert hingegen stark mit dem jeweils verwendeten organischen Lösungsmittel und mit den Konzentrationsparametern der wässrigen Ausgangslösung.

Allen Systemen ist gemeinsam, dass die Extrahierbarkeit des Indiums bei gegebenem Kaliumjodidgehalt der wässrigen Ausgangs-Lösung deutlich von deren Acidität abhängt (Abb. 2).

Bei der Extraktion des Indiums mit Diäthyläther ist dieser Einfluss der Schwefelsäurekonzentration auch noch bei hohen Kaliumjodidgehalten (1 Mol/l.) merklich. Erst bei Säuregehalten oberhalb 0,5 Val/l. lässt sich das Indium aus solchen Lösungen vollständig extrahieren. Demgegenüber erreicht die Extrahierbarkeit des Indiums bei Verwendung von Cyclohexanon als Lösungsmittel schon bei einem Kaliumjodidgehalt von 0,1 Mol/l. sehr bald einen konstanten, von der Schwefelsäurekonzentration unabhängigen Grenzwert. Dieser Grenzwert liegt bei Vorlage von 100 mg In in 50 ml (=0,0175 Mol/l.) bei etwa 95%. Diese unvollständige Extraktion ist eine Folge des unter den vorliegenden Bedingungen nur geringen Kaliumjodidüberschusses. Theoretisch könnten hier bei vollständigem Umsatz zu $[InJ_4]^-$ maximal etwa 140 mg Indium extrahiert werden. Bei grösserer Kaliumjodidkonzentration steigt die Extrahierbarkeit rasch auf 100% an und wird zugleich praktisch unabhängig vom Schwefelsäuregehalt der wässrigen Phase (Kurve 3b, 3c, 3d in Abb. 2). Ebenso steigt die Extrahierbarkeit bei konstanter Kaliumjodid- und Schwefelsäurekonzentration mit abnehmender Indiummenge an (Abb. 3).

Die Wirksamkeit von Isobutylmethylketon als Extraktionsmittel liegt zwischen denjenigen von Diäthyläther und von Cyclohexanon.

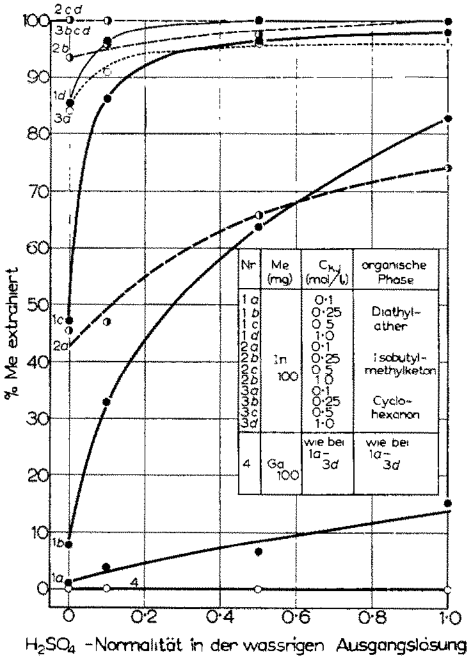

ABB. 2. Die Extrahierbarkeiten von Gallium und Indium in Abhängigkeit vom Schwefelsäuregehalt der wässrigen Ausgangslösung (Phasenverhältnis V_0/V_w = 50 ml/50 ml)

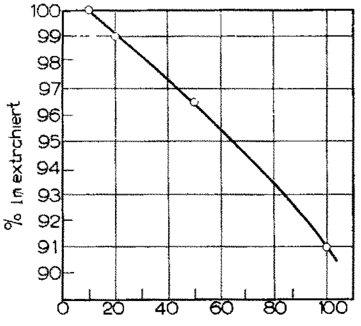

ABB. 3. Die Extrahierbarkeit von Indium mit Cyclohexanon aus 0,1 n schwefelsauren 0,1 m Kaliumjodidlösungen als Funktion der vorgelegten Indiummenge. (Phasenverhältnis V_0/V_w = 50 ml/50 ml).

Der funktionelle Zusammenhang zwischen der Extrahierbarkeit von Indium und dem Kaliumjodidgehalt der wässrigen Ausgangslösung bei konstanter Acidität nimmt einen ähnlichen Verlauf (Abb. 4).

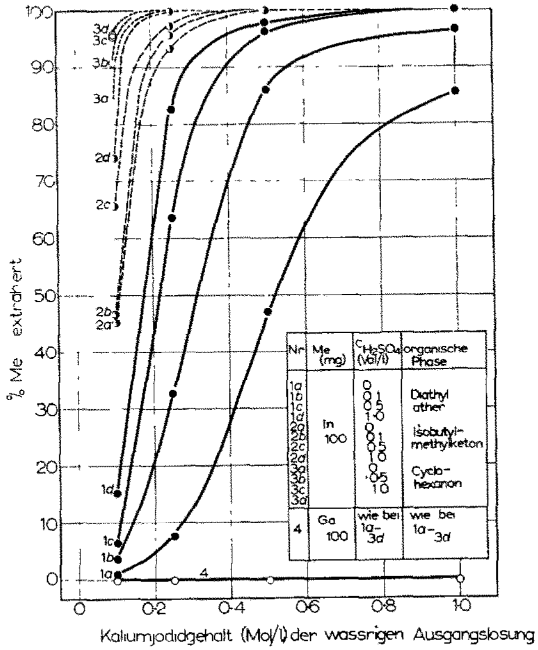

Abb. 4. Die Extrahierbarkeiten von Gallium und Indium in Abhängigkeit vom Kaliumjodidgehalt der wässrigen Ausgangslösung (Phasenverhältnis V_0/V_w = 50 ml/50 ml).

Auch hier ist zu erkennen, dass man eine vollständige, von den Konzentrationsparametern der wässrigen Ausgangslösung weitgehend unabhängige Indiumextraktion nur mit Cyclohexanon als Lösungsmittel erreicht. Isobutylmethylketon ist weniger gut geeignet.

Die Trennung des Indiums vom Gallium durch Extraktion aus wässrigen Kaliumjodidlösungen mit Cyclohexanon ist nicht nur vollständig, sondern auch gut reproduzierbar. Dies zeigen die beiden nachstehenden Messreihen (Tabelle II).

Aus den vorstehend geschilderten Untersuchungen ergibt sich folgende Arbeitsvorschrift für die extraktive Abtrennung des Indiums vom Gallium:

Zu der mindestens 0,2 n schwefelsauren Probenlösung, die keine merklichen Mengen von Chloriden und Bromiden enthalten darf, gibt man Kaliumjodid in einer solchen Menge hinzu, dass ein 6–10 facher molarer Überschuss gegenüber dem vorhandenen Indium erreicht wird. Dann extrahiert man etwa 2–3 min lang mit einem gleichen oder grösseren Volumen Cyclohexanon, lässt die Phasen sich trennen und bestimmt das Gallium in der wässrigen Phase in gewohnter Weise. Das in der organischen Phase quantitativ enthaltene Indium kann nach Abdampfen des Lösungsmittels durch Fällung als Indium(III)-hydroxyd und Wägung als Indiumoxyd bestimmt werden. Nach demselben Verfahren können auch die Erdalkalien, Aluminium und Eisen durch eine Extraktion von Indium getrennt werden.

TABELLE II

	I	II
Anzahl der Bestimmungen	25	11
Vorgelegte Indiummenge (Mittelwert)	109,1 mg	98,64 mg
Vorgelegte Galliummenge (Mittelwert)	18,53 mg	99,00 mg
Volumen der wässrigen Phase	50 ml	50 ml
C_{KJ} (wässrige Phase)	0,125 n	0,25 n
$C_{H_2SO_4}$ (wässrige Phase)	0,125 n	0,1 n
Volumen der organischen Phase	50 ml	50 ml
Gefundene Indiummenge (Mittelwert)	108,7 mg	98,49 mg
Standardabweichung	±0,66 mg	±0,60 mg
Gefundene Galliummenge (Mittelwert)	18,49 mg	99,33 mg
Standardabweichung	±0,07 mg	±0,42 mg

Summary—The influence of the organic solvent on the indium-gallium separation from iodine-containing aqueous solutions has been investigated.

The known extraction of indium with ether can be considerably improved by using higher ketones. The extraction with *cyclo*hexanone is especially effective. Even at very small iodide concentrations and low acidity the separation factor is greater than 10^4. The alkaline earths, aluminium and iron can be separated from indium in a single extraction by the same procedure. Indium is extracted by *cyclo*hexanone as the tetraiodo-indate, $(InI_4)^-$.

Résumé—L'auteur a étudié l'influence du solvant organique sur la séparation Indium-gallium à partir de solutions aqueuses contenant de l'iodure.

L'extraction connue de l'indium par l'éther peut être considérablement améliorée en utilisant des cétones à longue chaine.

L'extraction par la cyclohexanone est particulièrement efficace. Même pour des concentrations d'iodure très petites et une faible acidité, le facteur de séparation est supérieur à 10^4. Les alcalino-terreux, l'aluminium et le fer peuvent être séparés de l'indium par une seule extraction utilisant le même procédé. L'indium est extrait par la cyclohexanone sous forme de tetraiodo-indate $(InI_4)^-$.

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STUDIES ON MATERIALS CONTAINING URONIC ACID—I

AN APPARATUS FOR ROUTINE SEMI-MICRO ESTIMATIONS OF URONIC ACID CONTENT

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Summary—The design features of some of the many forms of apparatus previously proposed for the estimation of uronic acids using the Lefèvre and Tollens decarboxylation reaction have been critically examined. Several sources of error have been eliminated, and a simple, yet reliable, apparatus facilitating routine estimations on a semi-micro scale has been developed. Details of the experimental procedure and apparatus finally devised are given.

IN recent years, carbohydrate chemists have shown an ever-increasing interest in polyuronides and acidic polysaccharides of plant and animal origin. Having carried out during previous investigations many uronic acid estimations on a wide variety of polysaccharide fractions,[1,2,3] the author found, in common with several other workers in this department, that reasonably reproducible results were not easily obtained, even when 250 to 500 mg samples were taken and a facsimile of the apparatus described[4] by McCready, Swenson and Maclay was used (cf. ref. 5). Non-homogeneity of samples was ruled out since the same difficulty was found with pure standards. As the method also gave an unsatisfactorily large and variable "blank", it was considered that, in addition to the well-known sources of error arising from lack of specificity of the reaction, certain errors were present in the experimental procedure. A critical study of some of the many forms of apparatus previously published was therefore made with the intention of devising a simplified apparatus having the following fundamental features: (*a*) no unnecessary joints and traps, (*b*) no "blank", (*c*) reproducible results from semi-micro samples, (d) ease of use for routine analyses and for kinetic studies of the decarboxylation reaction.

It was found that more than 100 papers on the decarboxylation reaction have been published. No recent critical review appears to be available. Several analytical methods other than that based on the classical decarboxylation reaction exist; these, and the reasons why there is often lack of agreement between the values they give, have been discussed.[5,6,7,29]

A multiplicity of colorimetric methods has been described, based on such reagents as (*a*) naphthoresorcinol[8,9,10] (*b*) anthrone[11,12] (*c*) carbazole[13,14,15] (*d*) thioglycollic acid[16] and (*e*) alkaline hydroxylamine.[17] Very recently, a method based on ultra-violet estimation of the degradation products resulting from heating with concentrated H_2SO_4 has been proposed.[18] Such colorimetric methods are often useful in micro-scale analyses, although they are not based on quantitative reactions,[29,30] and many conflicting reports regarding their specificity and validity exist.[8,9,12]

In addition the accuracy obtainable, detailed procedures involved, and time required per analysis make these methods no more advantageous for routine determinations than the classical decarboxylation reaction, several adaptations of which for micro-scale analyses have been described.[19,20,21,22] No known method for determination of uronic acids is entirely selective;[23,24] *estimations* only are possible at present. Nevertheless, it was considered that elimination of all apparatus errors, subsequent critical study of the reaction kinetics and mechanism, and an investigation into possible methods of minimising the amounts of CO_2 evolved from (*a*) undesirable side reactions (*b*) non-uronic acid materials, could increase the accuracy and specificity of the decarboxylation method. A preliminary note[25] has indicated the extent of the investigations already carried out: various aspects will be reported as subsequent parts of this series elsewhere in due course. This paper deals only with the description of the apparatus and analytical method evolved, a preliminary account of which was given during its development.[26]

EXPERIMENTAL

(1) *Choice of decarboxylation agent*

The use of 19% (w/w) aqueous HCl as decarboxylating agent was introduced[4] with the claim that decarboxylation was complete in 1½–2 hours at an oil-bath temperature of 145°, as opposed to the 4–5 hours required with 12% HCl. Since a method suitable for routine analyses was under development, the use of 19% HCl was retained. (The claims of several authors[27,28] that use of 19% HCl leads to less accurate estimations is now being investigated.)

(2) *Choice of scavenging, with introduction of by-pass system*

The apparatus was designed for scavenging by a slow stream (pressure stabilised at 15 ml/min) of CO_2-freed "spot" nitrogen, rather than by sucking through CO_2-free air. (Recently, indications that the small content of oxygen in "spot" nitrogen may affect the course of the reaction in certain cases have been obtained. A study of this effect is in progress.) A scavenging by-pass system, operated by two 2-way taps, was designed; this greatly facilitates routine operation.

(3) *Design of titration cell for* CO_2 *absorption*

Choice of method for estimating the CO_2 evolved was difficult. The iodometric method[24] (which is insensitive to traces of HCl retained by the carrier-gas), potentiometric titration,[29] and gravimetric[31,32,33] methods were all considered, but the titrimetric method, which is the most convenient for routine use, was retained. A trap permitting addition of all reagents directly into a nitrogen atmosphere was designed. *Quantitative* absorption of CO_2 *at twice the flow-rate normally used in analyses* was proved (*a*) by fitting a similar cell to the exit as a guard-tube (*b*) by trapping the exit gas at $-180°$ and testing for CO_2 by an infra-red technique which has been described.[36]

(4) *Elimination of all unnecessary traps and joints*

Zinc dust,[4] mossy zinc,[34] aq. $AgNO_3$,[35] Ag_2SO_4 paste,[19] and water[24,28] traps have been used to remove traces of HCl carried over by the scavenging-gas. Maher,[27] however, found such traps unnecessary if a long reflux condenser was used. This was confirmed, provided (*a*) low flow-rates were used (10–15 ml/min), (*b*) the carrier-gas inlet did not reach below reflux level in the reaction flask. To keep the overall size and internal volume of the apparatus small, further experiments were conducted using a fairly short ether-type condenser. Blank determinations and infra-red analyses showed no escape of HCl even at flow-rates twice that normally used. The same infra-red analyses showed that *non-methylated* uronic-acids, hexoses, pentoses and polysaccharides gave CO_2 + furan as the volatile reaction products. Pure furfural was refluxed under the analytical conditions used; only traces of furan (no furfural) were detected in the scavenging-gas. It has been stated[37] that refluxing furfural for 2 hours in 19% HCl destroys 60%, whilst steam distillation gives 99% recovery of the furfural: under the conditions of low flow-rate, non-aeration of reaction mixture, and high reflux efficiency used in this analytical method no furfural is volatilised. Furan gives no reaction in the

CO_2 absorption trap. The aniline or phloroglucinol scrubber included in previous methods was thus eliminated, and the design of a compact, single-unit, apparatus having only one critical joint was possible.

(5) *Heating of reaction-flask*

In numerous previous methods, heating by oil-bath maintained at 135–145°, or even higher, was used. 19% HCl refluxes at about 109° and bath temperatures much in excess of this were found to produce charring on the reaction-flask walls, with resultant evolution of spurious and non-reproducible quantities of CO_2. This effect also results if heat is directly applied to a level higher than that of the refluxing liquid inside the flask. Complete elimination of such charring was achieved by heating the 100-ml flask with an electrothermal mantle designed for 50-ml flasks. The heat available just maintains reflux, and the flask area to which heat is applied is suitably limited.

Construction of apparatus

The apparatus is shown to scale in Fig. 1. It is readily constructed by a competent glass-blower. The ether-type condenser has two concentric coils wound closely round a central vertical conductor. The outer coil is a sliding fit inside the outer wall, and the concentric coils fit closely inside each other.

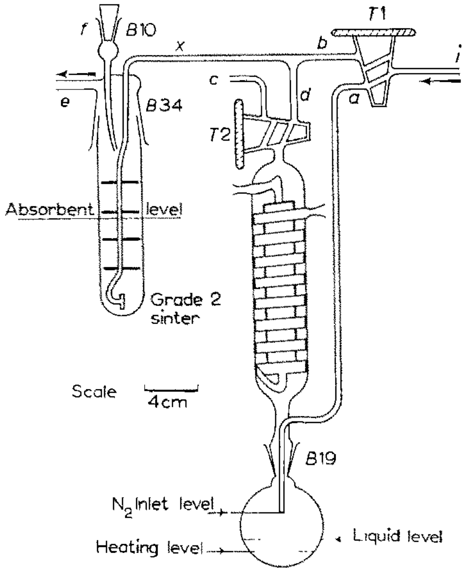

FIG. 1.

The condenser jacket is virtually filled with cooling coils, and the internal volume of condenser and absorption trap is only 150 ml. Since decarboxylation requires about 2½ hr for completion, a flow-rate faster than 15 ml/min is unnecessary. The absorption-trap is constructed from a B34 cone and socket. About 50% of the ground-glass cone is cut off; this permits a closer fit of the baffle plates inside the absorption-tube. Baffles can be made either of glass (the Q. and Q. "Disc Distributor EX10/20" supplied with Soxhlet extractors is easily adaptable), or of thin polythene discs, in which a central hole and radial slot are cut to permit a tight fit on the delivery tube, which ends in a 1-cm diameter sinter-disc. A space left between this disc and the bottom of the tube allows the coagulated $BaCO_3$ ppt. to settle. Grade 2 porosity is the most suitable; a stream of fine bubbles is desired without creation of a back-pressure great enough to test either the B19 joint on the reaction-flask or the taps T_1 and T_2. Several discs may have to be made before one fulfilling these conditions is obtained; the average pore-size usually decreases with heating and annealing. For kinetic measurements, a two-way junction stop-cock system is introduced at *x* in Fig. 1, so that the gas stream can be switched through different traps. A pair of traps fitted with closely matched sinter-discs is then essential, otherwise differing back-pressures are created, which, it was found, alter the reflux temperature sufficiently to affect reaction rates.

At the start of an analysis, sufficient time is allowed for nitrogen to scavenge the apparatus and trap. 15·00 ml of 0·05*N* $Ba(OH)_2$ is then added at *f* from a CO_2-free storage system, and the delivery-tube *f* washed down until the absorbent level in the trap is just below the third baffle. The baffles create turbulence, so that quantitative absorption of CO_2 is achieved and the absorbent concentration remains uniform. A slight pumping action develops and the third baffle is kept awash. The top baffle acts as an anti-spray device. When absorption is complete, back-titration of excess $Ba(OH)_2$ to phenolphthalein end-point is possible by addition of 0·05*N* HCl from a burette *via f*. Adequate trap volume remains if care is taken with the quantity of wash-water used. Turbulence inside the trap produces homogeneity within about 1 minute. Excellent end-points are obtainable with a little care: should the end-point be exceeded, direct titration of the slight excess of acid can in turn be made.

Routine operation sequence

The apparatus is permanently held by clamps round the B34 socket of the absorption-cell and round the condenser. The pressure-stabilised flow of carefully purified "spot" nitrogen, regulated by needle valves and rotameter at 15 ml/min, enters the apparatus at *i*. The reaction-flask containing the weighed sample and 35 ml of 19% HCl is placed in position. A trace of silicone grease is used; a good joint is essential. T_1 and T_2 are positioned so that nitrogen flows through *a* and out at *c*. After 10 minutes (or longer as considered necessary if carbonate is suspected in the sample) the condenser will have been swept out, and T_2 is turned so that the nitrogen flows through *d*. Heating of the reaction-flask is begun. When reflux begins (after about 10 minutes) the trap will have been swept out (with no stopper in position at *f*). 15 ml of 0·05*N* $Ba(OH)_2$ etc. are now added as already described; the first traces of CO_2 from the decarboxylation will not reach the trap until 10 minutes later. When decarboxylation is complete, T_1 is turned so that nitrogen flows through *b* and through the trap. T_2 is turned to release the slight pressure inside the reaction-flask and condenser through *c*. The heating-mantle and flask are removed, and a second flask containing sample II positioned. The absorption trap contents are now back-titrated, and T_1 is then turned so that nitrogen flows through *a* to *c*. Whilst the reaction-flask and condenser are thus being swept, the absorption trap is lowered, thoroughly rinsed and replaced. T_2 is then turned to position *d*, heating is begun, and the cycle of operations completed as already described.

The by-pass system therefore ensures that the steady flow-rate need never be interrupted (important in kinetic studies) and that the minimum time is lost between analyses. Three analyses can be completed in 8 hours, and the apparatus needs no attention during each 2½ hours decarboxylation period.

RESULTS

CO_2-free distilled water and *AnalaR* grade chemicals are used; reagents are stored in vessels protected with Sofnolite guard-tubes. The standard analytical conditions are:— Flow-rate = 15 ml/min; Vol. of 19% (w/w) HCl used = 35 ml; reflux temp. = 108–109°; decarboxylation time = 2½ hrs from start of reflux; sample weights sufficient to liberate 1–5 mg CO_2 are preferable, but 0·5 mg CO_2 can be determined without loss of accuracy (see Table II).

1. *"Blank" determinations*

(*a*) No blank is given under standard analytical conditions.

(*b*) 50 ml 19% HCl refluxed continuously *for 96 hrs* at *25* ml/min flow-rate gave:— (1) acidity absorbed in $Ba(OH)_2$ $\not>$ 0·02 ml 0·05*N*. (2) CO_2free distilled water, initially colourless to phenolphthalein, turned very faint pink. (3) alkalinity absorbed in HCl $\not>$ 0·02 ml 0·05*N*.

2. *Determination on National Bureau of Standards "Dolomite 88"* (% CO_2 = *47·25*)

A reaction flask fitted with a side-arm dropping-funnel for addition of acid was used. Wt. of sample taken = 12·48 mg. CO_2 found = 47·1%. First traces of cloudiness in $Ba(OH)_2$ trap appeared 12 minutes after first addition of acid. Liberation of CO_2 was fast, but infra-red analysis (sensitive[36] to 0·2 mg CO_2) showed that absorption of CO_2 was complete.

3. *Determinations on standards*

Uronic acid standards of 100% purity are difficult to obtain. Glucurone (American Corn Products Refining Co. Ltd.) once recrystallised, and having Neutralisation Equivalent = 171 (mean of 5 detns.), and galacturonic acid monohydrate (Roche Chemicals Ltd.), were used to obtain the results shown in Table I.

TABLE I

Sample	% purity found from neut. equivt.	Apparent % uronic acid found,							
		Decarboxylation time, *mins*							
		20	40	60	90	120	150	240	480
Glucurone	97·2*	57·0	80·2	86·7	94·3	95·6	96·7 97·2 97·4 96·8	98·3	101·5
Galacturonic acid monohydrate	96·0†	73·0	89·0	92·1	93·8	95·0	95·8 95·4 95·6	98·5	103·0

* Calculated as uronic acid anhydride.
† Calculated as monohydrate.

A decarboxylation period of 2½ hours is therefore used in routine analyses. In this time, the CO$_2$ evolved from non-uronic materials varies from apparent uronic acid anhydride contents of 3·5% for pure L(+)rhamnose and D(+)mannose to 1·8% for D(+)glucose and D(+)xylose. A full account of the kinetic results obtained and their detailed application to the method of analysis wll be given as a later part of this series.

4. *Results obtained for Hakea gum samples**

TABLE II

		Wt. taken *mg*	CO$_2$ found *mg*	% Uronic acid anhydride
Crystalline Hakea gum.	Detn. 1	116·85	3·35	11·4
	2	110·71	3·06	11·1
	3	103·20	2·88	11·2
	4	70·72	1·98	11·2
	5	48·23	1·35	11·4
	6	21·00	0·59	11·2
Fractionated Hakea gum.	Detn. 1†	35·05	4·73	56·2
	2	23·61	3·31	56·0
	3	11·63	1·64	56·4

* Prepared by Dr. A. M. Stephen, Univ. of Cape Town.
† Neut. Equivt. subsequently found (by Dr. A. M. Stephen) = 315, *i.e.* % Uronic acid anhydride = 55·8.

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Zusammenfassung—Die Eigentümlichkeiten von einigen der vielen zur Bestimmung der Uronsäure mittels der Lèfevre und Tollens-Dekarboxylation-Reaktion schon vorgeschlagenen Apparat-Typen werden kritisch untersucht. Mehrere Fehlerquellen sind eliminiert worden und ein einfacher, zuverlässiger Apparat, der Normal-Bestimmung auf einer Halb-mikroskala erleichert, wurde entwickelt. Die Nebenumstände des experimentellen Verfahrens und des vorgeschlagenen Apparats werden angegeben.

Résumé—Les caractéristiques de quelques uns des nombreux appareils proposés jusqu'ici pour la détermination des acides uroniques en utilisant la réaction de décarboxylation de Lefèvre et Tollens ont été examinés d'un point de vue critique. Plusieurs sources d'erreur ont été éliminées et un appareil simple, cependant fidèle, permettant les déterminations de routine à l'échelle semi-micro a été proposé. On donne le détail des conditions expérimentales et de l'appareil tel qu'il a été conçu finalement.

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POLAROGRAPHIC DETERMINATION OF DIBUTYL PHTHALATE IN PROPELLANT COMPOSITIONS CONTAINING NITROGLYCERINE*

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Summary—The direct polarographic determination of dibutyl phthalate in propellant compositions containing nitroglycerine is not readily practicable by normal polarography because of the marked interference of the nitroglycerine which gives polarographic steps preceding those of the dibutyl phthalate, making quantitative work very difficult. This necessitates a preliminary chromatographic separation of the nitroglycerine and dibutyl phthalate before polarography. Dibutyl phthalate can be determined directly in the presence of nitroglycerine by means of the cathode-ray polarograph. Up to a certain value of nitroglycerine there is an enhancement of the height of the peak used for the determination of dibutyl phthalate and this is accompanied by a gradual increase in the peak potential of the dibutyl phthalate. Above this value there is no further change so that it is ensured that the nitroglycerine content of the sample is above this level before carrying out the analysis. The accuracy of the method is of a good order.

A DIRECT chemical procedure which has been described for the determination of dibutyl phthalate in the presence of nitroglycerine, is based on saponification of the ester after removal of the nitroglycerine with ammonium sulphide.[1] This procedure is somewhat lengthy and unpleasant.

Phthalate esters have been determined polarographically by Whitnack and Gantz[2] who showed that they are reduced in a base solution consisting of 25 % aqueous 0·1*M* tetramethylammonium chloride with 75 % of a non-aqueous solvent such as ethanol or acetone. It was considered that it might be possible to apply the polarographic method to propellant mixtures containing, among other constituents, nitroglycerine in addition to dibutyl phthalate.

The particular class of propellants in which we were interested, had the following composition:

	%
Ethyl centralite	6–7·5
Nitroglycerine	32·75–35·75
Mineral jelly	0·1–0·4
Dibutyl phthalate	7·5–9·0
Nitrocellulose (and chalk)	48·5–50·5
Potassium nitrate	0·5–1·5

Experiments were carried out on the ether extract from the propellant. This contained mineral jelly, ethyl centralite, nitroglycerine, dibutyl phthalate and probably a little nitrocellulose. Employing the conventional polarograph it was not possible to determine the dibutyl phthalate directly on the ether extract because nitroglycerine

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gave a large preceding wave which interfered with that from the dibutyl phthalate, and it was therefore necessary first to separate the nitroglycerine. It was possible to do this by a chromatographic technique which unfortunately considerably lengthened the method, and, in addition, introduced sources of error which affected the figure obtained in the final polarographic determination of dibutyl phthalate. In view of this, further work was carried out using the more sensitive cathode ray polarograph. It was found that, though nitroglycerine had an enhancing effect on the height of the dibutyl phthalate trace obtained on the oscillograph, it did not affect the linear relationship between the concentration and peak height for dibutyl phthalate. It was found, moreover, that above a certain level of concentration of nitroglycerine, after subtracting a small "blank" due to nitroglycerine, the peak height obtained for dibutyl phthalate was independent of the nitroglycerine concentration. It was thus possible to determine the dibutyl phthalate directly in the presence of nitroglycerine; in addition, it could be determined in the presence of the other ether-soluble constituents of the propellant. After removing the ether from the propellant extract in a suitable apparatus, the residue was dissolved in methanol, suitably diluted and an appropriate portion polarographed in the manner described below. The results obtained were in close agreement with those obtained by carrying out carefully controlled analyses by a difference method.

METHOD

(1) *Reagents*

Ether: pure dry ether.

Methanol: pure anhydrous methanol.

Standard dibutyl phthalate solution: dissolve 0·25 g dibutyl phthalate in 250 ml of methanol in a standard flask.

Standard nitroglycerine solution: dissolve 1 g of nitroglycerine in 500 ml of methanol in a standard flask.

Standard solution of nitroglycerine and dibutyl phthalate: take sufficient of the dibutyl phthalate standard solution to give a known concn. of about 100 μg/ml when diluted to 50 ml with methanol and then add sufficient nitroglycerine solution such that the ratio of dibutyl phthalate to nitroglycerine present is of the same order as that in the sample itself. This amount of nitroglycerine should be at least the minimum amount of nitroglycerine to give the maximum enhancing effect (see p. 83) on the dibutyl phthalate wave. The final volume of methanol solution should be equal to 50 ml.

Standard nitroglycerine "blank" solution: prepare a solution of nitroglycerine in 50 ml of methanol so that it contains the same amount of nitroglycerine as present in the standard butyl phthalate-nitroglycerine solution.

0·2M tetramethyl ammonium iodide solution: dissolve 4 g of tetramethyl ammonium iodide, which has been recrystallised five times from water, in 100 ml of water.

(2) *Extraction procedure*

Weigh accurately about 1 g of the propellant sample into a sintered-glass crucible and extract with ether in a suitable extraction unit for six hours. Evaporate the resulting solution to dryness in a current of dry air taking the usual precautions for handling materials containing nitroglycerine. Dissolve the residue in methanol and dilute it to 100 ml in a standard flask. Dilute 10 ml of this solution to 100 ml with methanol and use the resulting solution for the polarographic determination of the dibutyl phthalate.

(3) *Polarography using the cathode-ray polarograph**

Transfer 10 ml of the methanol solution containing the dibutyl phthalate into a suitable glass-stoppered flask and add 10 ml of the tetramethyl ammonium iodide solution. Thoroughly mix the

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* The Cathode-Ray Polarograph used in this work was from Southern Instruments Limited.

solutions and transfer a suitable amount to a polarographic cell. Place the cell in position on the polarograph stand and connect to it a nitrogen bubbler containing equal volumes of methanol and water. Pass a stream of nitrogen, first through the bubbler and then through the cell at a rate of three bubbles per second for exactly five minutes. Disconnect the nitrogen and polarograph the solution in the usual manner. A well defined peak due to the dibutyl phthalate trace will appear at a potential of about −1·52 v (mercury pool). Measure the vertical height from the base line to the peak and then repeat the whole procedure taking 10 ml of the standard solution. Finally carry out a "blank" determination using 10 ml of the standard nitroglycerine "blank" solution, measuring the vertical height of the trace at the peak potential of the dibutyl phthalate. In each case take the mean of 3 determinations.

(4) *Calculation of results*

Let a = the peak height of the unknown solution from which the nitroglycerine "blank" has been deducted.

Let b = the peak height of the standard solution corrected for the "blank" as above.

Then the concentration x in μg/ml of dibutyl phthalate in the cell is given by

$$x = \frac{a \times 50}{b}$$

If the weight of propellant taken is y g, then the percentage of dibutyl phthalate in the propellant sample is given by

$$\frac{2x}{10y}$$

1. *Indirect determination of dibutyl phthalate by chromatography followed by polarography*

The normal polarographic behaviour of constituents of propellants which were considered likely to interfere with the determination of dibutyl phthalate were nitroglycerine, ethyl centralite, mineral jelly and possibly nitrocellulose. It was soon found that only the nitroglycerine presented an interference problem. The solubility of the nitrocellulose in the initial ether extraction was too small to give sufficient nitrocellulose to cause interference. Nitroglycerine was found to give polarographic steps occurring at potentials of approximately 0·2, 0·4 and 0·7 volts; there was considerable interference with the dibutyl phthalate wave 1·5 v which followed (see Fig. 1). A Tinsley Polarograph was employed for this work. It was considered that a preliminary chromatographic fractionation might serve as a means for separating the dibutyl phthalate from the nitroglycerine.

Ovenston[3] and Schroeder[4] have done a considerable amount of work on the separation of propellant constituents using silica gel-Celite 535 mixtures as adsorbents. We have extended this technique to the quantitative separation of dibutyl phthalate from nitroglycerine. A column of silica gel-Celite (3 : 1) was prepared in a solvent consisting of benzene-ligroin (3 : 1) using about 25 g of adsorbent in a glass tube 2 cm in diameter. The solid residue obtained from the ether extract of the propellant was dissolved in 5 ml of the solvent mixture and transferred to the column. The nitroglycerine and mineral jelly were extracted with 300 ml of the solvent mixture and the dibutyl phthalate and ethyl centralite were then removed using 150 ml of ethyl ether. After evaporating off the ether on a water bath, the residue was dissolved in 200 ml of methanol. A volume of 5 ml of this solution was taken together with 5 ml of 0·1M tetramethyl ammonium iodide base electrolyte, and a suitable maximum

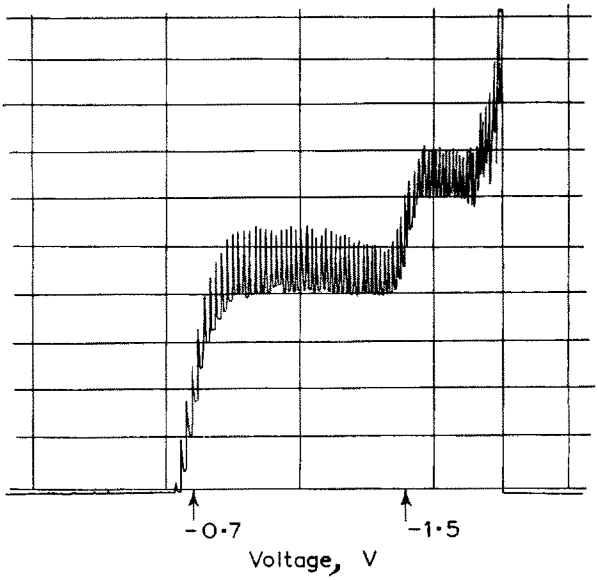

FIG. 1.—Polarogram obtained from dibutyl phthalate on Tinsley pen-recording polarograph in the presence of nitroglycerine.

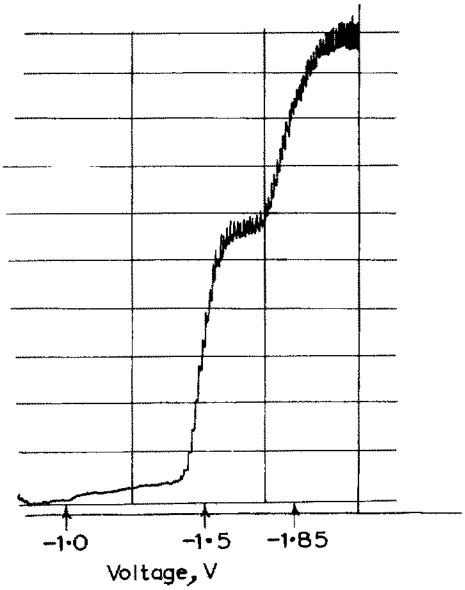

FIG. 2.—Polarogram obtained from dibutyl phthalate on Tinsley pen-recording polarograph, direct reading.

suppressor (*e.g.* methyl red) was added. The solution was polarographed in the normal way. It will be seen that there are two waves (see Fig. 2) which appear at half wave potentials of —1·5 v and —1·85 v respectively. The first wave was used in these analyses.

RESULTS

1. *The direct determination of dibutyl phthalate using the cathode-ray polarograph:*

In view of the fact that the chromatographic-polarographic technique was time consuming and more liable to random errors, the polarographic behaviour of dibutyl phthalate was examined using the more sensitive cathode-ray polarograph.

(a) *The dibutyl phthalate trace.* The solutions employed consisted of a standard solution of dibutyl phthalate in methanol mixed with an equal volume of 0·2*M* aqueous tetramethylammonium iodide. Dibutyl phthalate gave two peaks at —1·52 v and —1·83 v respectively (Fig. 3; *cf.* Fig. 2). In the work which follows that appearing at a peak potential of —1·52 v was used.

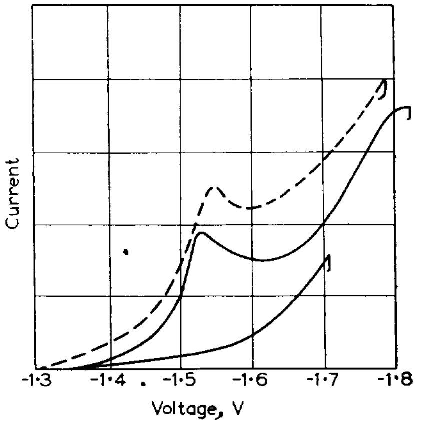

FIG. 3.—Polarogram obtained from dibutyl phthalate on cathode-ray polarograph. The broken line shows the effect of nitroglycerine on the dibutyl phthalate trace. The lower line shows the trace due to the nitroglycerine "blank" solution.

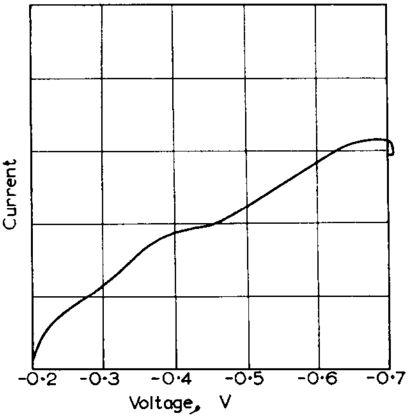

FIG. 4.—Polarogram obtained from nitroglycerine on cathode-ray polarograph.

As was expected, ethyl centralite and mineral jelly were not reduced and caused no interference.

Nitroglycerine gives a final peak at a potential of about —0·7 v (Fig. 4). Since the solution obtained from the propellant extract was expected to contain of the order of 72 μg/ml of dibutyl phthalate and 340 μg/ml of nitroglycerine, subsequent work was carried out using solutions containing around these concentrations.

(b) *Effect of nitroglycerine on the peak potential of dibutyl phthalate:* It was found that nitroglycerine had a slight effect on the peak potential of dibutyl phthalate, the potential "increasing negatively" with increasing nitroglycerine concentration. Table I shows the effect of increasing nitroglycerine concentration on the value of the peak potential of dibutyl phthalate.

TABLE I.—THE EFFECT OF NITROGLYCERINE ON THE "PEAK POTENTIAL" OF DIBUTYL PHTHALATE

Nitroglycerine concentration in cell, *μg/ml*	Peak potential of dibutyl phthalate, *v*
0	—1·520
40	−1·525
80	−1·530
120	—1·540
160	−1·550
200	—1·555
240	—1·555

It was considered that the peak occurring at the potential of —1·52 v could form the basis of a quantitative procedure for dibutyl phthalate but it would be necessary to investigate the effect of a number of possible interferences.

(c) *Effect of nitroglycerine on peak height of dibutyl phthalate:* In the absence of nitroglycerine, the height of the dibutyl phthalate peak is directly proportional to the amount of dibutyl phthalate present. The peak height was however appreciably affected by the nitroglycerine. In the absence of dibutyl phthalate, blank values were obtained by polarographing methanol solutions containing various concentrations of nitroglycerine in the manner described on p. 80. The height of the trace was measured at the appropriate peak potential (see Table I) and the results are shown graphically in Fig. 5.

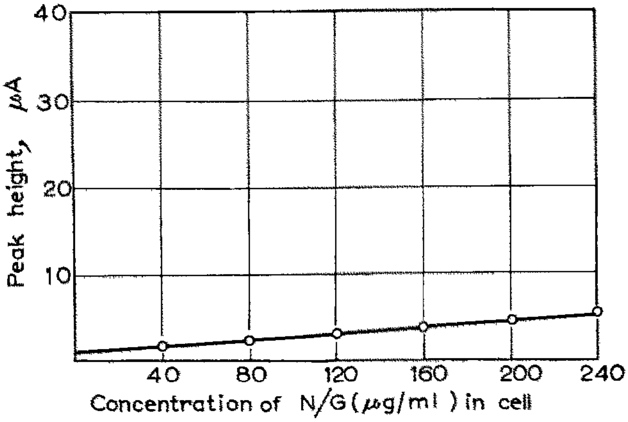

FIG. 5.—Polarographic behaviour of nitroglycerine in the method for dibutyl phthalate.

(d) *Effect of nitroglycerine on the peak height of dibutyl phthalate:* It was found that, while ethyl centralite and mineral jelly had no effect on the dibutyl phthalate peak height, nitroglycerine enhanced it. This effect is not due solely to the additive effect of the "blank" values and it reaches a maximum, after which it is constant. The solutions used for polarography contained 50 μg/ml and 40 μg/ml dibutyl phthalate respectively in a 1 : 1 mixture of methanol and water, 0·1*M* with respect to tetramethylammonium iodide, along with various concentrations of nitroglycerine.

(e) *Effect of nitroglycerine on the linearity of the dibutyl phthalate concentration versus peak height curve:* Above about 80 μg/ml of nitroglycerine, change in concentration of the nitroglycerine does not appreciably affect the slope of the curve for the linear relationship between the peak height and concentration of dibutyl phthalate, provided the "blank" value is subtracted from the peak height.

(f) *Determination of dibutyl phthalate in synthetic solutions:* Synthetic solutions were made up containing 340 μg/ml nitroglycerine and various concentrations of dibutyl phthalate. These solutions were mixed with equal volumes of 0·2*M* aqueous tetramethylammonium iodide and polarographed. Employing a standard solution containing 100 μg/ml dibutyl phthalate and 340 μg/ml nitroglycerine mixed with an equal volume of 0·2*M* aqueous tetramethylammonium iodide the amount of dibutyl phthalate present in each solution was determined by the procedure described on p. 80. The results obtained are given in Table II. They show that excellent recoveries of the dibutyl phthalate are obtained above 30 μg/ml of base solution. Below this level, experimental error becomes more significant.

TABLE II.—THE DETERMINATION OF DIBUTYL PHTHALATE IN SYNTHETIC SOLUTIONS

Dibutyl phthalate added in cell, *μg/ml*	Dibutyl phthalate found in cell, *μg/ml*
14	15·1
18	19·0
19	21·1
21	21·3
30	30·2
31	31·0
35	34·8
39	38·9
42	43·2
44	45·5
51	50·8
52	52·9

TABLE III.—THE DETERMINATION OF DIBUTYL PHTHALATE IN A PROPELLANT

Dibutyl phthalate recovered, %	
(*a*) By polarograph	(*b*) By difference
7·65	7·8
7·70	7·8
7·79	7·7
7·88	8·0
8·00	8·1

(g) *Determination of dibutyl phthalate in propellant samples:* Various samples of propellant (1 g) of the general type of composition given on p. 79 were extracted with ether for six hours, and the ether was evaporated off and the residue dissolved in 100 ml methanol; a volume of 10 ml of this solution was diluted to a further 100 ml with methanol and this solution was used for polarography. Results are given in Table III. They show excellent agreement with results obtained by very careful determinations carried out by the difference procedure.

DISCUSSION

Dr. F. A. HOLTON, Hammersmith Hospital, London asked whether it was likely that the dibutyl phthalate which was added to the mixtures which were to be analysed was quite free from other organic phthalates. It was necessary to know this since the polarographic method would be unlikely to distinguish between the different phthalates and of course different phthalates may behave differently in the propellant mixture.

In his reply Mr. Williams said that the type of organic phthalate present in the mixture would affect the behaviour of the propellant. Since the propellants are made within fairly close limits some clue would surely be obtained from the figure obtained for the result as to whether or not the particular phthalate had been added. Usually, of course, for routine control of the industrial process the particular phthalate used would be known. Further of course, the method would not distinguish between isomers such as *iso* and *normal* dibutyl phthalate.

Dr. R. J. MAGEE, Queen's University, Belfast asked whether a comparison had been made between results obtained using the cathode-ray polarograph and a method using chromatography which removes nitrocellulose, followed by conventional polarography. The question is raised because of the possibility that the nitrocellulose would affect the wave-height of the phthalate.

Mr. Williams replied by pointing out that in the preliminary treatment of the propellant an ether extraction is carried out which removes only dibutyl phthalate, nitroglycerine, mineral jelly and ethyl centralite so that the question of interference by nitrocellulose would not, of course, arise. It has however been shown that the method still applies in the presence of very small amounts of nitrocellulose.

Mr. G. RUSSELL, Ilford Limited, suggested that the enhancement effect due to nitroglycerine might be caused by adsorption of the nitroglycerine and this could possibly be tested by adding something which was known to be very strongly adsorbed *e.g.* gelatine.

Mr. Williams agreed that this was a distinct possibility and said that he would carry out a few experiments on the lines suggested by Mr. Russell.

Mr. Williams asked Mr. R. C. ROONEY, British Cast Iron Research Association whether he had encountered any similar "enhancing" phenomena on the cathode-ray polarograph. Mr. Rooney replied that in the case of the aluminium-solochrome violet complex different slopes were obtained for different dyestuffs concentrations. Mr. Rooney had ascribed this to viscosity effects but this explanation may not be correct. Mr. Rooney pointed out that he had also obtained some depressing effects on the cathode-ray trace.

Mr. G. L. YOUNG, Cambridge Instrument Company asked whether it was possible that the reduction products of nitroglycerine affected the wave-height of the phthalate ion. If not, could not a controlled potential electrolysis method be used in order to remove the nitroglycerine.

Mr. Williams agreed that this was something that should be investigated but a further stage such as Mr. Young had suggested would, of course, lengthen the method and detract from its use in routine operation.

Zusammenfassung—Die direkte polarographische Bestimmung von Dibutyl-Phthalat in nitroglycerinhaltigen Treibstoffen ist wegen der ausgeprägten Interferenz von Nitroglycerin, das polarographische Stufen liefert, die denjenigen von Dibutyl-Phthalat vorausgehen und quantitatives Arbeiten sehr erschweren, mit Hilfe der normalen Polarographie nicht leicht durchführbar. Dies macht eine chromatographische Trennung von Nitroglycerin und Dibutyl-Phthalat vor dem Polarographieren notwendig. Man kann Dibutyl-Phthalat bei Anwesenheit von Nitroglycerin mittels eines Kathodenstrahl-Polarographen bestimmen. Bis zu einem gewissen Gehalt von Nitroglycerin gibt es eine Verbesserung für die zur Bestimmung von Dibutyl-Phthalat gebrauchte Stufenhöhe. Dies wird durch eine langsame Steigerung des Stufenpotentials von Dibutyl-Phthalat begleitet. Über diesem Gehalt gibt es keine weitere Änderung, und daher hat man sich zu vergewissern, dass der Nitroglycerin-gehalt der Probe über diesem Wert ist, bevor man die Analyse durchführt. Die Methode erwies sich als genau.

Résumé—Le dosage direct du dibutyl phthalate dans les compositions propulsives contenant de la nitroglycérine par polarographie normale est peu praticable par suite des fortes perturbations apportées par la nitroglycérine, qui donne des paliers polarographiques avant ceux du dibutyl phthalate, ce qui rend très difficile le dosage quantitatif. Une séparation préliminaire par chromatographie de la nitroglycérine d'avec le dibutyl phthalate est donc nécessaire avant le dosage polarographique.

On peut doser directement le dibutyl phthalate en présence de nitroglycérine au moyen du polarographique à rayons cathodiques. Jusqu'à une certaine valeur de nitroglycérine il y a lieu une augmentation du maximum utilisé pour déterminer le dibutyl phthalate; celli-ci est accompagnée d'une augmentation progressive du maximum du potential du dibutyl phthalate. Au-dessus de cette limite il n'y a plus de variation; on s'assure donc, avant d'effectuer l'analyse, d'une teneur en nitroglycérine qui dépasse cette limite. La méthode est précise.

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SHORT COMMUNICATIONS

Apparatus for titrations using ultraviolet light

(*Received* 28 *July* 1958)

ULTRAVIOLET illumination has been applied as a means of exciting fluorescent radiation which is useful for the identification and determination of inorganic and organic materials. Many fluorescent pH indicators have been described.[1] Their use, however, has been confined to specialized problems. The fluorescent pH indicators are used advantageously for acid-base titrations in highly coloured solutions.

The analogous application of fluorescent indicators has not been taken advantage of for chelometric titrations. This is surprising in view of the difficulties encountered with chelometric methods because of the formation of highly-coloured complexes.

The apparatus shown in Fig. 1 was designed in order to facilitate chelometric titrations with ultraviolet light as the sole source of illumination.

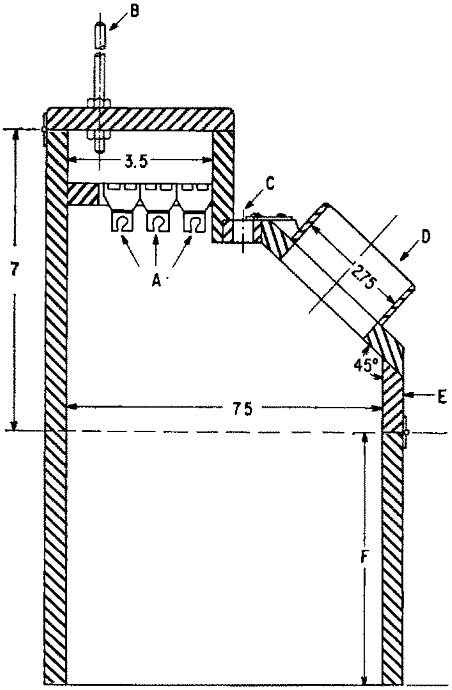

FIG. 1. Section through apparatus for fluorescent titrations.
(The arrows, A, indicate the lamp sockets, since the lamps are in the direction perpendicular to the plane of the paper.)

The shell of the apparatus is constructed of one-half-inch plywood and is painted a dull black. The top is hinged to give access to the "black light" fluorescent lamps (A) which are mounted on a removable "U" frame to facilitate their replacement. The lamps are wired with separate switches (not shown) so as to enable the selection of three intensities of fluorescent radiation. A burette is mounted to the rod (B) and centred over the one-half-inch diameter hole (C). The tip of the burette is removed and a piece of 1/16 × 1/16-inch rubber tubing used to extend the burette through the hole (C). The tubing is cut and the tip from the burette inserted so as to extend the burette to an appropriate height above the beaker. The hole (C) is sealed adequately by slitting a one-inch length of 3/16 × 1/8-inch tubing and placing it around the burette extension tubing. This permits a rapid change in burettes so that various titrants may be used simply by removing the burette and inserting another. In addition a flexible burette extension eliminates the danger of breaking a burette through careless removal of a beaker. The viewing slot (D) is 2.75 inches wide (as shown in Fig. 1) and 6.25 inches long. The ends of (D) are rounded and the outside dimension has a slight taper to facilitate the use of an oscilloscope viewing-hood over the entire viewing hole. The viewing-hood is shortened so that distance from the eye to the plane of the hinged door (E) is about 9½ inches. A magnetic cabinet-latch is mounted inside to hold the door (E) closed. The bench top serves as a bottom to make the interior adequately light-tight. Titrations are most conveniently carried out with a magnetic stirrer controlled externally with a Variac. The distance (F) should be equal to the distance from the bench top to the top of the magnetic stirrer. The length (inside) of the apparatus in the plane perpendicular to Fig. 1 is 13 inches. This length accommodates 8-watt fluorescent lamps (General Electric F8T5B1B), which have a rated output of 760 fluorens each. The openings (C) and (D) are centred on this length.

The apparatus has been applied to chelometric titrations using EDTA and triethylenetetramine. These applications will be the subject of subsequent investigations of the use of fluorescent indicators in chelometric titrations.

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[1] *Organic Chemical Bulletin, Fluorescent Indicators*, 1957, **29**, No. 4.

The use of molecular filter membrane in mounting and assaying of radioactive precipitates*

(*Received* 26 *August* 1958)

A COMMON operation in radiochemical analysis is the mounting of radioactive precipitates in a deposit sufficiently uniform for precise counting. The support on which the material is deposited must not interfere with accurate weighing of the mounted precipitate. The filtration method of collecting a precipitate on a filter-disc is widely used since it is more rapid than techniques involving evaporation of slurried suspension and yields more uniform deposits.

In a recent communication, Bloom[1] made reference to the advantages of using filter paper as a supporting material for quantitative assay of active precipitates. However, low precision has been obtained in weighing mounted deposits of 10–30 mg, and it is attributed to uncertainties in the tare weights of filter paper discs. Filter paper readily absorbs atmospheric moisture, and reflects in its weight variations in the humidity of the laboratory, despite the use of a desiccator. Further, it has been found that filter paper discs decrease permanently in weight following the heating required for drying moist deposits (15–20 mins at 120°).

Alternatively, molecular[4] filter membrane such as the cellulose material manufactured by Millipore Corp. is a suitable material for filtering and weighing precipitates. The material is quite constant in weight despite heating or exposure to moist air. In the table below the relative weights of filter paper and Millipore filter-discs and their weight losses on heating are indicated. The thin Millipore disc, which has superior filtration characteristics, weighs only 4–5 mg. cm^{-2} compared to 15–20 mg. cm^{-2} for a Whatman No. 42 filter paper disc.

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* Issued as A.E.C.L. No. 428 and declassified A.E.C.L. report CRDC-687.

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* Issued as A.E.C.L. No. 428 and declassified A.E.C.L. report CRDC-687.

TABLE I. WEIGHT LOSSES ON HEATING FILTER-DISCS

Filter Material	Disc diam., *in.*	Initial wt. of disc, *mg*	Wt. after 15 min heating at 120°, *mg*	Wt. after 30 min heating at 120° *mg*
Filter paper disc (Whatman No. 42)	$1{\cdot}12_5$ $1{\cdot}12_5$	$135{\cdot}4_8$ $132{\cdot}4_5$	$134{\cdot}1_4$ $131{\cdot}1_1$	$133{\cdot}6_5$ $130{\cdot}6_2$
Filter paper disc + AgI precipitate	$1{\cdot}12_5$	131·22	$142{\cdot}9_0$ (disc + ppt.)	$141{\cdot}3_2$ (disc + ppt.)
Millipore filter disc (H.A. assay type)	1·00	$15{\cdot}1_7$	$15{\cdot}1_5$	$15{\cdot}1_4$
Millipore filter disc + AgI precipitate	$1{\cdot}12_5$	25·10	$49{\cdot}5_8$ (disc + ppt.)	$49{\cdot}5_5$ (disc + ppt.)

The weight loss resulting from thirty mins heating at 120° is barely detectable with Millipore discs, but amounts to 1·5–2 mg per paper disc. An uncertain weight loss of this magnitude can introduce errors of 5–10% in the analysis of 10–30 mg of precipitate on a filter paper support.

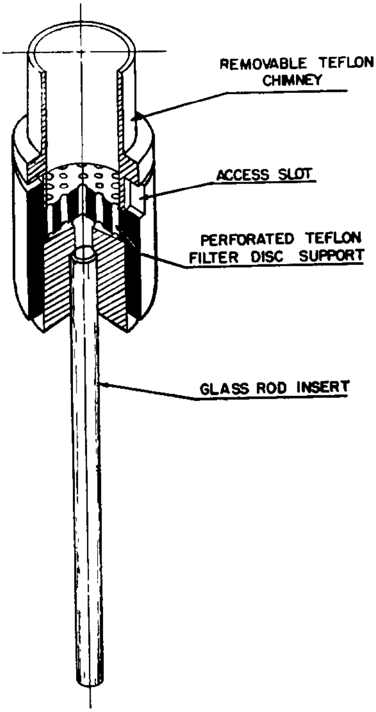

FIG. 1. **Filtration assembly**

Thin sheets of the synthetic material are highly retentive, and in spite of its fine porosity, the material offers very little flow resistance so that solutions may be rapidly filtered. These features of molecular filters are of importance in rapid radiochemical analyses for short-lived nuclides since the resulting precipitates are often incompletely coagulated and not readily filterable.

Because of these several advantages, Millipore filter-discs have been used in our laboratory in radiochemical analysis for some time with a three-fold improvement in the precision of specific activity measurements. The only disadvantages involved in its use are (*a*) a lower mechanical strength of the thin sheet compared to fibrous type filters and (*b*) solubility in some organic solvents: methanol, esters and ketones such as acetone which are useful for quick-drying moist precipitates. Petroleum ether may be used for quick-drying without attacking the filter-disc.

Various types of demountable Hirsch and modified Büchner funnels for collecting precipitates on filter-discs have been described.[2,3] A readily assembled filtration apparatus has been designed in our laboratory (see Fig. 1) to support 1⅛-in diameter Millipore filter-discs for filtration of liquid suspensions. The assembly, machined from Teflon, is free of one of the common problems encountered with glass and porcelain filtration apparatus: since solutions do not "wet" the surfaces of the plastic assembly there is little tendency for precipitates to "creep" up the walls of the chimney or for solutions to leak past the filter-disc around the lower edges of the chimney. The filter-disc is held firmly in place by the close-fitting chimney assembly on a perforated plate. It is necessary to distribute the suction uniformly to avoid spotty, non-uniform deposits. This may be accomplished by supporting the filter-disc on one of the nutrient pads supplied by the manufacturer with the filters for use in bacteriological analysis.

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PRELIMINARY COMMUNICATIONS

A new spot test for the detection of fluoride ion

(*Received* 29 *October* 1958)

AVAILABLE colour tests for the detection of fluoride ion are based on the bleaching of a coloured metal complex, or on the liberation of a free dyestuff from a differently coloured metal chelate through the formation of a more firmly bound, colourless metal-fluoride complex.

We have found that the fluoride ion produces a coloured complex with the cerium^{III} chelate of alizarin complexone[1] (1:2-dihydroxyanthraquinonyl-3-methylamine-N:N-diacetic acid). In an acetate buffer the red colour of the cerium^{III}-alizarin complexone changes to the lilac-blue colour of the double complex; the reaction forms a suitable basis for a sensitive spot test for the detection of fluoride ion (the colour of alizarin complexone at the same pH is yellow). The mechanism of the reaction and the nature of the new complex are being studied and will be described in a later publication. To the best of our knowledge this is the only reaction of the fluoride ion in which it is itself responsible for the production of a *new* coloured species.

The test is remarkably free from interference from other common anions. The quantitative basis of the reaction is now being studied and will also be reported on at a later stage. Since cerium^{III} is the only metal amongst those we have examined which is capable of giving the colour reaction with alizarin complexone and fluoride ion, there is little doubt that a spot test could also be devised for detection of cerium^{III}. The tervalent rare earths were not examined in this investigation but would probably behave as cerium.

The fluoride test is carried out in an acetate buffer at pH 4·3. The order of addition of reagents is important in that a much quicker colour response is obtained if the alizarin complexone and cerium^{III} ion are added separately to the fluoride ion rather than as a composite solution of the cerium^{III} chelate.

Interference with the fluoride test

The interference tests were carried out at the limit of fluoride concentration which permitted unequivocal identification of the ion, *viz.* 0·2 μg.

Anions: A 100-fold excess (molecular proportions) of the following anions did not interfere with the colour produced by 0·2 μg of fluoride ion: sulphide, sulphate, thiosulphate, chloride, bromide, iodide, cyanide.

In addition, substances such as mannitol and dihydroxyethylglycine, *i.e.* weak organic complexing agents, did not interfere.

A six-fold excess of the following ions partly inhibited the colour reaction: phosphate, and intermediate strength organic complexing agents such as iminodiacetic acid.

Oxalate, citrate and tartrate, uramildiacetic acid and EDTA, *viz.* strong organic chelating agents, completely inhibited the colour reaction of the fluoride ion when present in amounts equal to the fluoride ion. They interfere by removing the cerium itself from the alizarin complexone, thus inhibiting even the formation of the red cerium^{III} chelate. The interference of these ions can readily be overcome, provided that they are not present in excessively large amounts, by adding sufficient cerium^{III} to the test solution to provide sufficient concentration of *free* cerium^{III} ions for the reaction with alizarin complexone and fluoride.

Cations: Certain heavy metals, *e.g.* Al^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+} and Zn^{2+} prevented the formation of the blue fluoride complex when present in amounts equivalent to the fluoride ion concentration.

A ten-fold excess of calcium caused a slight inhibition of the colour formation whereas 100-fold excesses of other metals, *e.g.* Hg^{2+}, Mn^{2+}, Mg^{2+} had no visible effect on the test.

Procedure

Place a drop of the test solution in the depression of a spot plate together with a drop of 0·001*M* alizarin complexone lightly buffered at pH 4·5 with sodium acetate-acetic acid. To this mixture add with immediate stirring, one drop of 0·001*M* cerous nitrate solution. Compare the colour developed at the end of one minute with that produced by the reagents alone, using one drop of distilled water in place of the test solution.

If the test solution contains fluoride ion, a lilac-blue colour will develop which may be compared with the scarlet-red of the alizarin complexone-cerous chelate. When only minute amounts of fluoride are present the spot plate should be viewed in diffuse daylight to facilitate the detection of the blue shade in the solution. Also, slight dilution with water of both the test and blank spots may improve visibility.

Limit of Identification	0·2 μg
Dilution Limit	0·2 μg in 0·36 ml *i.e.* 1 in 1,800,000

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New reagents for the detection of technetium

(*Received* 5 *November* 1958)

GERLIT,[1] in discussing some chemical properties of technetium, has indicated that the chemical, and especially the analytical properties of the element are comparatively little known. Indeed, apart from the radiochemical counting method usually employed, the limited detection of technetium can only be achieved by two or three known reagents. Tetraphenylarsonium chloride and nitron[2] have been used as precipitating reagents for the element, but suffer from the great disadvantage that they react in a similar way with rhenium. No other suitable reagent appears to have been developed.

In connection with work on the separation of manganese, technetium, rhenium and ruthenium carried out in this department, which will be reported in the near future, it was found necessary to develop a sound and reliable non-radiochemical procedure for the detection of very small amounts of the technetium. This paper reports the results obtained in this investigation.

EXPERIMENTAL

A number of reagents were investigated under varying conditions of acidity. The most promising of these are shown in Table I.

TABLE I

Reagent	Medium	Oxidation state of technetium	Observations
Potassium thiocyanate	Acidic	IV	Purple to pink colours
Potassium thiocyanate + stannous chloride	Acidic	IV, VII	Yellow colour
Dimethylglyoxime + stannous chloride	Acidic	IV, VII	Green colour
Nitron	Slightly acidic	VII	White precipitate
Tetraphenylarsonium chloride	Acidic	VII	White precipitate
Thiourea	Acidic	VII	Orange colour
Potassium xanthate	Acidic	IV, VII	Purple colour

Procedure

Place a drop of the test solution in the depression of a spot plate together with a drop of 0·001*M* alizarin complexone lightly buffered at pH 4·5 with sodium acetate-acetic acid. To this mixture add with immediate stirring, one drop of 0·001*M* cerous nitrate solution. Compare the colour developed at the end of one minute with that produced by the reagents alone, using one drop of distilled water in place of the test solution.

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Of these reagents, the most satisfactory were potassium xanthate, dimethylglyoxime + stannous chloride, potassium thiocyanate in hydrochloric acid, and thiourea in nitric acid.

Potassium xanthate

A saturated aqueous solution of the reagent was prepared. In solutions containing mineral acids, Tc^{IV} or Tc^{VII} (pertechnetate) yield a purple-red coloration with the reagent. This coloration is readily extractable into chloroform or carbon tetrachloride. In neutral or alkaline solution no red coloration is obtained with the reagent. Rhenium, manganese and ruthenium do not react, and do not therefore interfere, but molybdenum gives a similar reaction. Apart from molybdenum, however, the reaction appears to be specific for technetium, among a range of some 20 ions examined. Because of the limited quantity of technetium available for investigation the tests were carried out on the ultra-micro scale, using techniques described elsewhere.[3,4]

Procedure: Treat 10 mμl of the test solution with about 50 mμl of potassium ethyl xanthate solution (sat. aq.) Add about 50 mμl of 2*N* HNO_3 or 2*N* HCl. An immediate pink to purple coloration (the shade depending on the concentration of technetium) is produced. Centrifuge. Add approximately 40 mμl of carbon tetrachloride and centrifuge once more. The colour passes into the carbon tetrachloride layer at the bottom of the centrifuge cone, leaving a colourless aqueous layer above. The limit of identification is 0·02 μg Tc.

Dimethylglyoxime + stannous chloride

The reagents are a saturated solution of dimethylglyoxime in 95% ethanol and 15–30% stannous chloride in 10*N* HCl. In the test a green coloration is produced in the presence of Tc^{IV} or Tc^{VII}. It would appear that the stannous chloride reduces the element to a lower oxidation state which can form a complex with the dimethylglyoxime, since there is no reaction in either of the above states in the absence of stannous chloride. The test appears likely to be specific for technetium, no other element among 20 tested producing this coloration under the conditions of experiment. We hope to investigate this reaction for the colorimetric determination of technetium.

Procedure: Add approximately 100 mμl of the dimethylglyoxime reagent to a cone containing about 100 mμl of the test solution. Then add about 50 mμl of the stannous chloride solution. A violet to green colour rapidly changing to a bright green colour is obtained, and this latter colour is stable even at the boiling temperature of the solution. On standing the colour is still stable after more than two weeks. The limit of identification is 0·04 μg Tc.

Thiourea in nitric acid

A 10% aqueous solution of thiourea is used. This is an excellent and sensitive method for detecting technetium as pertechnetate. Therefore when Tc^{VII} is not present the solution is oxidised by means of 2*N* nitric acid to produce this form. In the presence of technetium an orange to red colour forms on heating. This colour is very stable on standing, and will be investigated for the colorimetric determination of Tc^{VII}. Rhenium, manganese and ruthenium do not interfere with the test.

Procedure: To approximately 100 mμl of the test solution add 50 mμl of 2*N* nitric acid followed by the same volume of 10% aqueous thiourea solution. Warm the solution for 2–3 minutes at 80°. The appearance of an orange-red colour confirms the presence of technetium. The limit of identification is 0·04 μg Tc.

Potassium thiocyanate in hydrochloric acid

The reagent used is a 20% aqueous solution of potassium thiocyanate. In a solution made acidic with 6*N* hydrochloric acid, technetium as Tc^{IV} reacts with the reagent to give a pink to purple colour. This colour is stable even on boiling, and is not extractable from the aqueous phase by carbon tetrachloride or chloroform. Tc^{VII} produces no such colour with the reagent. Great care was taken to ensure that traces of Fe^{III} were not the cause of the colour produced.

Procedure: To about 100 mμl of the test solution add 50 mμl of 6*N* hydrochloric acid followed by 40 mμl of potassium thiocyanate reagent. Heat in boiling water for 5 minutes. A persistent pink to purple colour confirms the presence of Tc^{IV}.

Note: The addition of stannous chloride in 10*N* hydrochloric acid to this purple solution produces a deep yellow colour. Direct reduction of Tc^{VII} with stannous chloride in the presence of thiocyanate produces a similar yellow colour.

Acknowledgement—The authors are indebted to Professor R. S. Nyholm of University College, London for the loan of 1 milligram of technetium which made the current work possible.

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The solubility of hydrogen sulphide in water

(*Received* 5 *November* 1958)

In the course of work on the precipitation of metal sulphides[1] it was found that variable results were obtained under what were believed to be standardised conditions. For example, in one series of experiments in which arsenic pentasulphide was precipitated, hydrogen sulphide was absorbed under the pressure at which it was contained in the generator (a "Microid" H_2S or CO_2 generator manufactured by Messrs. Griffin and Tatlock, Ltd.). The gas was passed into a conical flask by means of a delivery tube terminating just above the surface of the $arsenic^{V}$ solution, and the exit-tube was sealed after having displaced the air in the flask; the flask was then shaken for 30 minutes. The amounts of precipitate obtained were extremely variable.

When this effect was further examined, it was found that the concentrations of hydrogen sulphide obtained after absorption in a similar way for a standard time into water and dilute acid were also very variable.[2] In some experiments in which hydrogen sulphide was bubbled at a fixed rate through water or dilute hydrochloric acid for periods of from 5 to 60 minutes, the eventual concentrations of hydrogen sulphide varied erratically and did not reach the accepted equilibrium value at the prevailing temperature[2–6] ($0{\cdot}12M$ at 20°). Generally, the higher the rate at which hydrogen sulphide was bubbled, the higher was its eventual concentration in solution; a similar observation had already been made by Belcher, Buchanan and Stephen.[2] It seemed therefore that the composition of the gas produced was varying with the rate of generation.

The generator was recharged with ferrous sulphide sticks and 1 : 1 HCl, and gas was generated at different rates. Periodically, samples of the gas produced were collected and treated with strong sodium hydroxide solution ($10N$), the diminution in gas volume being measured as an indication of the H_2S concentration. The residual gas was hydrogen.

After the last value recorded in the table, the generator was discharged at a rate of 60–65 ml/min (*i.e. ca* 4 bubbles/sec) until this rate began to diminish (after about 60 hours). The percentage of hydrogen sulphide was then 78·8%.

It can be seen from Table I that the higher the rate of generation, the purer was the hydrogen sulphide obtained. Exceptionally low hydrogen sulphide concentrations were obtained immediately after the generation had been interrupted overnight; but even in normal intermittent use, the gas a deep yellow colour. Direct reduction of Tc^{VII} with stannous chloride in the presence of thiocyanate produces a similar yellow colour.

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It can be seen from Table I that the higher the rate of generation, the purer was the hydrogen sulphide obtained. Exceptionally low hydrogen sulphide concentrations were obtained immediately after the generation had been interrupted overnight; but even in normal intermittent use, the gas contained less than 80% by volume of hydrogen sulphide. In particular, under conditions corresponding to those existing in qualitative analysis, only rarely were solutions 0·05*M* in hydrogen sulphide produced at room temperature.

Some further confirmation of this was sought in the literature and was found in the work of Kolthoff and Griffith.[6] These authors used less concentrated hydrochloric acid (3*N* compared with 5*N* here) in a Kipp generator; they found that the amount of hydrogen varied between 2 and 18%, and was as much as 20% at the start of a discharge. The purity of the hydrogen sulphide increased with the flow rate.

TABLE I

Time of discharge, *minutes*	Flow rate, *ml/min*	Time for which flow was stopped	% H_2S v/v
0–35	60–65		0
		9 mins	
35–110	60–65		14·2
		5 mins	
110–301	60–65		80·7
		5 mins	
301–356	60–65		82·5
		4 mins	
356–494	175–180		85·8
		4 mins	
494–641	60–65		82·1
		17 hours	
641–661	60–65		61·3
		4 mins	
661–772	175–180		89·3
		4 mins	
772–798	310–320		89·6
		18 hours	
798–836	60–65		51·0
		2 hours	
836–852	60–65		54·3
		36 mins	
852–869	60–65		63·2
		47 mins	
869–887	60–65		72·2
		37 mins	
887–923	60–65		77·8
		18 hours	
923–942	60–65		67·9

It is well-known that the conventional Mass Action calculations concerned with the precipitation of sulphides bear no resemblance to the values found experimentally[2] and this can be attributed in part to the fact that the solubility figure for hydrogen sulphide generally used is 0·1*M*, whereas in practice it is likely to be less than 0·05*M*. Many other factors must be considered, however, *e.g.* complex formation and corrected values for solubility products and the dissociation constants for hydrogen sulphide. This aspect of the work will be dealt with in a later communication.

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BOOK REVIEWS

Microdiffusion Analysis and Volumetric Error. E. J. CONWAY. 4th revised edition. Crosby Lockwood and Son Ltd., London, 1957. Pp. xviii + 465. 42s.

MOST analytical and biological chemists are familiar with the principles of microdiffusion analysis which have been developed and applied by Professor Conway during the last twenty years. It is, however, seldom appreciated that within this same space of time there are few other chemists who can claim to be the originators of a particular method of analysis which involves entirely novel principles; yet the Conway diffusion technique when first presented to the chemical world was just this.

Like most "acceptable" methods of analysis, microdiffusion analysis has stood up to the stringent tests of time, and has established itself by its diverse applications as a valuable microchemical tool. There can be no better testimonial to its value than that, and further comment by a reviewer is unnecessary.

The present edition, revised and expanded, follows the pattern of its predecessors. The third edition appeared in 1950 so that Professor Conway has been able to incorporate into the present text the results and experiences of a further seven years with the method. The book is again divided into three main parts, the first dealing with the apparatus and principles of microdiffusion analysis, the second with descriptions of methods using the standard units or microdiffusion cells and the third and last, but by no means least, dealing with the very important subject of volumetric error.

In his preface the author lists an impressive amount of new material which he has included in this revised edition and which must enhance the value of the book not only to those actively engaged on the techniques of microdiffusion analysis, but also to those who intend applying the methods for the first time. It is the responsibility of an author of a text-book to ensure that his readers are kept up to date on his subject by its periodic revision. Professor Conway maintains his high standing as an author in the present text, which should find its place next to the earlier editions on the shelves of every practising analyst, whatever branch of analysis he is primarily concerned with.

WILLIAM I. STEPHEN

Quantitative Analysis. W. CONWAY PIERCE, EDWARD L. HAENISH and DONALD T. SAWYER. John Wiley and Sons, Inc., New York: Chapman and Hall, Ltd., London, Fourth Edition, 1958. Pp. xiii + 497. 46s.

ALTHOUGH this is the fourth edition of the book, it is ten years since the last edition was published and many changes have been made, so it is virtually a new book. The most important change is the addition of a section devoted to instrumental methods, which has necessitated the omission of some classical methods.

Nearly half the space is devoted to the theories underlying the various analytical procedures and to the necessary calculations. All this is very clearly set out and the emphasis on calculations and on the evaluation of experimental measurements is very salutary for students. The equilibria involved in acid-base, precipitation and oxidation-reduction reactions are well explained.

The experimental parts contain careful instructions on the balance and on the calibration of weights and volumetric apparatus. Typical titrimetric determinations are illustrated by neutralisation methods, use of potassium permanganate, iodimetry and iodometry (terms which, for direct and indirect methods, respectively, might not be acceptable to the purist), oxidation by ceric and dichromate ions, determination of halide by silver nitrate and the use of EDTA for determination of hardness in water (but there is no discrimination between calcium and magnesium hardness).

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Gravimetric methods are preceded by introductory remarks on the physical state of precipitates, solubility, co-precipitation, peptisation and so on, and methods given as typical are the precipitation of silver chloride, ferric hydroxide, barium sulphate, magnesium ammonium phosphate and nickel dimethylglyoxime. As a *bonne bouche* the analysis of limestone is added.

Instrumental methods are illustrated by colorimetric analysis, potentiometric titrations and electrodeposition procedures.

All the foregoing, although very limited in actual methods, would form a good basis for a general course. Moreover, the printing, diagrams and binding are excellent and the Reviewer is disappointed at not being able to detect a single misprint!

The book appears to be admirably adapted to American teaching methods, but from a British point of view there are too many injunctions to consult the "instructor"; and the numerous questions and exercises, although very good in their way, take up a disproportionate amount of space. Finally, many of the "sources of error in titrimetric operations" should surely have been instilled into a student in his first week in a laboratory, for instance, loss by spilling in weighing or in transfer, errors in weighing and use of wrong indicator. "Faulty mixing of solutions after they have been diluted", although equally obvious, probably justifies emphasis, to judge from the Reviewer's experience of students at all stages.

A. D. MITCHELL

Qualitative Testing and Inorganic Chemistry. JOSEPH NORDMANN. John Wiley and Sons, Inc., New York, 1957. Pp. xii + 488. $6.25.

THIS book is difficult to place. It has many good features but attempts too much and therefore would probably not be acceptable as a text-book for teaching in the United Kingdom. However, it has a wealth of ideas which teachers could study with interest and profit.

The word "testing" in the title implies a rather mechanical and routine approach, but, although this seems to be to some extent inherent in the methods of large-scale teaching in American institutions, this book does try to inculcate a logical method.

A frontispiece gives the Periodic Table in the modern "long" form in such a way as to include a mass of information on the electronic structure of the atoms (which is amplified in a later table) and also a summary of the properties of the fundamental particles.

Before the actual "testing" is approached, there are chapters on, *inter alia*: equations; methods of expressing the concentration of solutions; spectra, with reference to electrons, atoms, bonds and molecules; Werner ions, as a background to subsequent matter, and with reference to the ideas of Sidgwick and Pauling; acid–base theories; reaction rates and equilibria; solubility and precipitation; hydrolysis; electrochemical cells; organic reagents for qualitative analysis; minerals, metals and crystals; apparatus. All these can obviously only be discussed very cursorily, but the treatment is clear and up to date.

Analysis is by the usual semimicro-methods, and under each element is given a very brief account of its occurrence and general chemistry. Tables are given of the equilibrium constants for most reactions normally used for the detection of the radicals. After the commoner elements, and under the title "Less familiar engineering metals," appear Li, Be, Ti, V, Zr, Mo, W, and U.

Dry tests come after all the tests for cations and anions, whereas most analysts would put them first; similarly, the warning as to removal of heavy metals before testing for anions comes much too late.

A rather unnecessary two pages are devoted to spot tests for the classification of stainless steels, but these refer only to the products of one company.

Ammonium phosphomolybdate is described as "slow forming" on a water-bath, but a properly prepared molybdate reagent will instantly produce a good precipitate in the cold.

After the more usual types of test there follow those for the detection of free chlorine in water, tetraethyl-lead in petrol, potassium in coffee, reducing sugars in beer, and aluminium and zinc in antiperspirants. There are also tests for marihuana and blood (but the rôle of peroxidase is not mentioned). Other short notes deal with animal and vegetable fibres and with inks, fluorescence, Gravimetric methods are preceded by introductory remarks on the physical state of precipitates, solubility, co-precipitation, peptisation and so on, and methods given as typical are the precipitation of silver chloride, ferric hydroxide, barium sulphate, magnesium ammonium phosphate and nickel dimethylglyoxime. As a *bonne bouche* the analysis of limestone is added.

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The book appears to be admirably adapted to American teaching methods, but from a British point of view there are too many injunctions to consult the "instructor"; and the numerous questions and exercises, although very good in their way, take up a disproportionate amount of space. Finally, many of the "sources of error in titrimetric operations" should surely have been instilled into a student in his first week in a laboratory, for instance, loss by spilling in weighing or in transfer, errors in weighing and use of wrong indicator. "Faulty mixing of solutions after they have been diluted", although equally obvious, probably justifies emphasis, to judge from the Reviewer's experience of students at all stages.

A. D. MITCHELL

Qualitative Testing and Inorganic Chemistry. JOSEPH NORDMANN. John Wiley and Sons, Inc., New York, 1957. Pp. xii + 488. $6.25.

THIS book is difficult to place. It has many good features but attempts too much and therefore would probably not be acceptable as a text-book for teaching in the United Kingdom. However, it has a wealth of ideas which teachers could study with interest and profit.

The word "testing" in the title implies a rather mechanical and routine approach, but, although this seems to be to some extent inherent in the methods of large-scale teaching in American institutions, this book does try to inculcate a logical method.

A frontispiece gives the Periodic Table in the modern "long" form in such a way as to include a mass of information on the electronic structure of the atoms (which is amplified in a later table) and also a summary of the properties of the fundamental particles.

Before the actual "testing" is approached, there are chapters on, *inter alia*: equations; methods of expressing the concentration of solutions; spectra, with reference to electrons, atoms, bonds and molecules; Werner ions, as a background to subsequent matter, and with reference to the ideas of Sidgwick and Pauling; acid–base theories; reaction rates and equilibria; solubility and precipitation; hydrolysis; electrochemical cells; organic reagents for qualitative analysis; minerals, metals and crystals; apparatus. All these can obviously only be discussed very cursorily, but the treatment is clear and up to date.

Analysis is by the usual semimicro-methods, and under each element is given a very brief account of its occurrence and general chemistry. Tables are given of the equilibrium constants for most reactions normally used for the detection of the radicals. After the commoner elements, and under the title "Less familiar engineering metals," appear Li, Be, Ti, V, Zr, Mo, W, and U.

Dry tests come after all the tests for cations and anions, whereas most analysts would put them first; similarly, the warning as to removal of heavy metals before testing for anions comes much too late.

A rather unnecessary two pages are devoted to spot tests for the classification of stainless steels, but these refer only to the products of one company.

Ammonium phosphomolybdate is described as "slow forming" on a water-bath, but a properly prepared molybdate reagent will instantly produce a good precipitate in the cold.

After the more usual types of test there follow those for the detection of free chlorine in water, tetraethyl-lead in petrol, potassium in coffee, reducing sugars in beer, and aluminium and zinc in antiperspirants. There are also tests for marihuana and blood (but the rôle of peroxidase is not mentioned). Other short notes deal with animal and vegetable fibres and with inks, fluorescence, chromatography, dithizone, and use of the microscope for differentiation between calcium and strontium as their sulphates and iodates.

Most references are to the Journal of Chemical Education but the coverage as a whole is international.

An amusing feature of the "problems" is afforded by several examples in which a certain Jackson P. Slipshod puts forward bright ideas which are superficially plausible, and the problem is to detect the fallacy.

A few errors have been noted: phosphorous (used several times for the element), Twsett, cannibus (for Cannabis) and Megm (for Negm).

Minor criticisms are made regretfully because the author adopts a refreshing outlook and has obviously devoted much thought to his teaching. The same thought devoted to this book might have eliminated a number of *trivia*.

A. D. Mitchell

Proceedings of the Congress on Modern Analytical Chemistry in Industry. The Society for Analytical Chemistry, W. Heffer and Sons, Ltd., Cambridge, 1958. Pp. vii + 244. 42s.

This bound volume contains the complete manuscripts, together with a record of discussions, of the lectures presented during this outstanding meeting held at the University of St. Andrews, June 24–28, 1957. The twenty-three subjects are organised within three sections: (I) Analysis in Modern Industry, (II) The Application of Some Newer Analytical Techniques in Industry, and (III) Developments in Analysis for New Problems in Industry.

Each section was opened with a Congress Lecture, in order, *Analytical Chemistry in Industry*, by Dr. J. Craik, *Analysis and Food*, by Dr. E. B. Hughes, and *New Analytical Reagents and their Applications in Industrial Plant-Control Operations*, by Professor G. F. Smith. Other talks in Section I dealt with analytical research in the Chemical Research Laboratory at Teddington and current practices in the iron and steel, electrical, gas, and pharmaceutical industries as well as the Department of the Government Chemist. Techniques described in Section II included emission, infrared, and ultraviolet spectroscopy, gas, liquid-liquid, liquid-solid and paper chromatography, X-ray diffraction, together with specialised measurements associated with foods, medicine and plastics. Uses of radioactive and stable isotopes, polarography and gas chromatography were outlined in Section III.

On the whole the book presents an excellent up-to-date picture of the role of the analytical chemist and of the application of modern analytical techniques in the major industries. The broad field of activity was aptly expressed by Dr. B. W. Bradford and Mr. D. L. Nicholson, *viz.*, "Analysis is an essential part of—(*a*) chemical research, (*b*) control of process operation in chemical manufacture, and (*c*) control to specification of chemical products." In most cases appropriate references are given so that the reader can obtain further details on the techniques described.

This reviewer was particularly impressed with the brief descriptions of uses of spectrographic and colorimetric methods in the iron and steel industry, X-ray diffraction in the electrical and food industries, and microbiological methods for specific analyses in food and medical research. Also noteworthy were accounts of applications and general discussions of gas chromatography, infrared spectroscopy, radiochemistry, and polarography. In the last named, emphasis was placed on square-wave and cathode-ray polarography with the potential given for square-wave polarography with synchronized sweep, radio-frequency and pulse polarography.

The papers serve as a good source of information on the utility of various chemical and instrumental procedures. They provide a convenient means for spotting techniques which may be applied to the solution of new problems. For this purpose inclusion in the book of a brief index listing the techniques discussed, with page references, would have aided the analytical chemist interested in reviewing applications.

The book will be particularly useful to organisations planning expansion of analytical activities or needing improved facilities.

John Mitchell, Jr.

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The book will be particularly useful to organisations planning expansion of analytical activities or needing improved facilities.

JOHN MITCHELL, JR.

Tables of Interatomic Distances and Configuration in Molecules and Ions. Compiled by H. J. M. Bowen, J. Donohue, D. G. Jenkin, Olga Kennard, P. J. Wheatley, D. H. Whiffen. Scientific Editor, L. E. Sutton. Assistant Scientific Editor, D. G. Jenkin. General Editors, A. D. Mitchell, L. C. Cross. Special Publication No. 11. London: The Chemical Society, Burlington House, W.1. 1958. 2 guineas. $6.00.

Talanta, 1959, Vol. 2, pp. 102-103, Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged:

Thursday 22 *January* 1959: **Chemical Society**, Bristol Area: **Royal Institute of Chemistry**, Bristol and District Section: **Society of Chemical Industry**, Bristol Section: *Safety in the Use and Disposal of Radioactive Materials:* Dr. B. A. J. LISTER, D.I.C., A.R.C.S., F.R.I.C. Chemistry Department, The University, Bristol. 6.30 p.m.

Monday-Friday 26–30 *January* 1959: **Louisiana State University Symposium**on *Modern Methods of Analytical Chemistry*. Baton Rouge, La.

Saturday 31 *January* 1959: **Society for Analytical Chemistry**, North of England Section. Annual General Meeting followed by *Synthetic Foodstuff Colours—Control of Quality*: H. E. STAGG, B.Sc., F.R.I.C. Engineers' Club, Albert Square, Manchester. 2.15 p.m.

Wednesday 11 *February* 1959: **Society for Analytical Chemistry**, Midlands Section. *Recent Advances in the Analytical Chemistry of Polymers.* Speakers from Fort Dunlop. The University, Birmingham, 3. 6.30 p.m.

Friday 20 *February* 1959: **Society for Analytical Chemistry**, Microchemistry Group. Annual General Meeting. Chairman's Address: D. F. PHILLIPS, F.R.I.C. London.

Tuesday 24 *February* 1959: **Society for Analytical Chemistry**, Physical Methods Group. *Analysis of Intact Samples.* Meeting Room of Chemical Society, Burlington House, London, W.1. 6.30 p.m.

Friday 27 *February* 1959: **Society for Analytical Chemistry**, Scottish Section. *Recent Advances in the Analytical Chemistry of Plutonium*: F. J. WOODMAN, B.Sc., A.R.I.C. Royal Society of Edinburgh, 22 George Street, Edinburgh, 2. 7.0 p.m.

Monday-Friday 2–6 *March* 1959: **Tenth Pittsburgh Conference** on *Analytical Chemistry and Applied Spectroscopy*: Exposition of Modern Laboratory Equipment. Pittsburgh, Pa.

Friday 13 *March* 1959: **Society for Analytical Chemistry**, Western Section: **Royal Institute of Chemistry**, South Wales Section. *New Techniques in Qualitative Analysis*: D. W. WILSON, M.Sc., F.R.I.C., Swansea.

Monday 24 *August–Saturday* 29 *August* 1959: **Polarographic Society**: The Second International Congress of Polarography will be held in the University of Cambridge, and will consist of Scientific Sessions (original papers, reviews and discussions), an Exhibition of Commercial Equipment, Demonstrations of Laboratory Apparatus, visits to local industry and places of interest, and social functions.

A supporting programme for ladies is being arranged.

The scientific programme will be divided into the following Sections—

1. Instrumentation. 2. Theory and Kinetics. 3. Analytical and Industrial Applications. 4. Fundamental Studies. 5. Biological and Medical Applications. 6. Miscellaneous.

There will also be four Plenary Lectures by World Authorities and six Section Lectures.

Contributions will be welcome and details should be submitted to G. F. REYNOLDS, M.Sc., F.R.I.C., Chemical Inspectorate, Ministry of Supply, C.36, Royal Arsenal, Woolwich, London, S.E.18, England.

Intention to submit a communication should be notified as soon as possible and in any case not later than March 31st, 1959, by which date a summary of not exceeding 200 words is also required. Preprints of all papers will be issued and final manuscripts must therefore be received not later than May 31st, 1959.

Requests for application forms and further details should be esnt to Mrs. B. LAMB, B.Sc., F.R.I.C., Chemistry Laboratory, Evershed and Vignoles, Corner of Iveagh Avenue, North Circular Road, London, N.W.10, England.

Sunday 30 *August–Saturday* 5 *September* 1959: **Society for Analytical Chemistry and Royal Institute of Chemistry**: A Summer School in Analytical Chemistry will be held at the School of

Pharmacy, Brunswick Square, London, W.C.1., consisting of three separate but concurrent courses covering instrumental organic analysis, modern inorganic analysis, and gas chromatography. Attendance is open to members of the Royal Institute of Chemistry or of the Society for Analytical Chemistry.

The *B.S.I.News* for November, 1958 lists among new standards B.S.3035, 1958, *General recommendations for the sampling of manganese ore*, which contains recommendations in line with international agreement relating to the sampling of the ore in freight wagons immediately before it is loaded into a ship, or immediately after discharge at the port of arrival: and B.S.3048, 1958, *Code for the continuous sampling and automatic analysis of flue gases: Indicators and recorders*, dealing with automatic instruments which give a direct indication or record of the composition of flue gases from industrial plant.

The latter standard is complementary to B.S.1756, *Code for the sampling and analysis of flue gases*, which covers manually operated instruments. It is prefaced by notes on the value of automatic instruments for combustion control. The various instruments are described with points relevant to their use. Amongst the instruments covered are thermal conductivity instruments, instruments depending on chemical absorption and chemical reaction, viscosity and density instruments, oxygen meters, and infra-red absorption instruments. Notes are included on the determination of dew point.

An amendment slip, No. 6 (reference PD 3192) has been issued to B.S.410, 1943, *Test sieves*, and an amendment slip, No. 1 (reference PD 3205) has been issued to B.S.598, 1958, *Sampling and examination of bituminous mixtures for roads and buildings*.

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

Talanta, 1959, Vol. 2, p. 104, Pergamon Press Ltd. Printed in Northern Ireland

BOOKS RECEIVED

Electroanalytical Chemistry: James J. Lingane. Second Edition. Interscience Publishers, New York and London, 1958. Pp. xiv + 669. $14.50. 109s.

Actas do XV Congresso Internacional de Química Pura e Aplicada, 1956. Volume I. Secretário-Geral do XV Congresso, Instituto Superior Téchnico, Lisboa, Portugal, 1957. Pp. 1028. Escudos 320$00 (for 3 Volumes): by Air Mail Escudos 330$00.

Analytical Chemistry in Nuclear Reactor Technology, 1st Conference, 1957. U.S. Atomic Energy Commission, Office of Technical Services, Department of Commerce, Washington, 25, D.C. Pp. vi + 256. $3.50.

Elementary Practical Organic Chemistry, Part 3: Quantitative Organic Analysis. Arthur I. Vogel. Longmans Green and Co., Ltd., London, 1958. Pp. xii + 645–840 + xxxii. 21s.

Chromatographic Techniques: Clinical and Biochemical. Ivor Smith. William Heinemann, Medical Books Ltd., 1958. 42s.

The Chemical Behaviour of Zirconium. Warren B. Blumenthal. D. Van Nostrand Company, New York and London, 1958. Pp. vi + 398. $11.00. 82s. 6d.

***p*-Bromomandelic Acid: Reagent for Zirconium.** E. J. Newman. Hopkins and Williams, Ltd., Essex, England. Monograph No. 36, 1958. 4 pp.

PAPERS RECEIVED

Wet Oxidation of Organic Matter Employing Mixed Perchloric and Sulphuric Acids at Controlled Temperatures and Graded High Potentials. Harvey Diehl and G. Frederick Smith: (9 *November* 1958).

Quantitative Evaluation of Chromatograms by Double Decomposition with Simple Radioactive Reagents—I: The Use of ^{131}Ag in Radiometric Estimation of Organic and Phosphoric Acids. Z. J. Zubrzycki, A. Z. Budzyński and I. G. Campbell: (13 *November* 1958).

A General Method for Measuring Solubilities of Gases in Liquids. Martin B. Smith: (13 *November* 1958).

New Colour Tests for the Larger Polynuclear Hydrocarbons. Eugene Sawicki and Roger Barry: (21 *November* 1958).

The Spectrophotometric Determination of Cerium in Fluoride Salts. J. C. White and R. F. Apple: (21 *November* 1958).

The Determination of Zirconium in High Temperature Alloys Using Xylenol Orange. K. L. Cheng: (24 *November* 1958).

An Electrochemical Separation Process for Use in Polarography. R. L. Faircloth: (27 *November* 1958).

Polarographic Examination of the Chelating Power of EDTA and Some Closely Related Chelating Agents. W. Hoyle and T. S. West: (11 *December* 1958).

The Early Preparation and Analytical Use of Hydrogen Sulphide. F. Szabadváry: (13 *December* 1958).

The Precipitation of Nickel^{III} sulphide from Acid Solutions by Thioacetamide. David F. Bowersox, Dwight M. Smith and Ernest H. Swift. (16 *December* 1958).

The Separation and Determination of Aluminium, Gallium, Indium and Thallium by Partition Chromatography. Robert J. Magee and Ian A. P. Scott. (23 *December* 1958).

The Separation and Semi-quantitative Estimation of Molybdenum, Manganese, Technetium, Rhenium and Ruthenium on the Ultramicroscale. Fadhil Jasim, Robert J. Magee and Cecil L. Wilson (28 *December* 1958).

Talanta, 1959, Vol. 2, pp. 105 to 108. Pergamon Press Ltd. Printed in Northern Ireland

THE GRAVIMETRIC SEMI-MICRO DETERMINATION OF PHOSPHORUS, AS QUINOLINE PHOSPHOMOLYBDATE, IN ORGANIC COMPOUNDS

T. R. F. W. FENNELL and J. R. WEBB
Royal Aircraft Establishment, Farnborough, Hants, England

(*Received* 19 *September* 1958)

Summary—A gravimetric finish has been applied to the semi-micro determination of phosphorus in organic compounds after fusion with sodium peroxide. It has been shown that the precipitate of quinoline phosphomolybdate prepared from 3 mg of phosphorus has the theoretical composition and that, using a special weighing technique, very precise results can be obtained. Two other weighing techniques are described which give results satisfactory for semi-micro work.

In a previous paper[1] a method was described for the semi-micro determination of phosphorus in organic compounds using a modified peroxide bomb fusion followed by precipitation of quinoline phosphomolybdate which was determined alkalimetrically.

Although Wilson[2] stated that the precipitate of quinoline phosphomolybdate could be used gravimetrically on the micro scale, no further interest in this method appears to have been shown. Brabson and Edwards[3] weighed the analogous oxine precipitate, but others using quinoline phosphomolybdate[4,5] have employed the volumetric finish. Wilson[2] claimed that the quinoline phosphomolybdate was of the correct composition when up to 1·75 mg of phosphorus were precipitated but found high and variable apparent molecular weights for precipitates obtained from 4·5 to 14 mg of phosphorus. The range required for semi-micro organic analysis is 2 to 3 mg. The gravimetric determination of phosphorus in this range has now been investigated. It was considered that a gravimetric finish would be preferable as difficulty was sometimes experienced with the titrimetric finish owing to atmospheric contamination.

EXPERIMENTAL

Oven-drying conditions: Thermogravimetric examination of the precipitate previously dried at 110° established that no decomposition occurred below a temperature of 370°. It was found that 15 minutes oven drying at 160° was sufficient for routine purposes but for the highest possible accuracy a drying time of 30 minutes is recommended.

Molecular weight of the precipitate

In this and subsequent work on standard phosphate solutions, a 0·01*M* solution of potassium dihydrogen phosphate was used. Ten ml of this solution contain 3·098 mg of phosphorus. Crucibles were weighed on a semi-micro aperiodic balance.

As Wilson's observation[2] that the precipitate is slightly hygroscopic was confirmed, a weighing technique designed to minimise this effect was used to establish the molecular weight of the precipitate. Two matched sintered glass crucibles (porosity 4) were washed with water, dried at 160° for 30 minutes and cooled in a desiccator for 30 minutes. They were then transferred to the balance pans and weighed *immediately*—the lighter crucible acting as tare. Precipitated quinoline phosphomolybdate[1] was filtered by suction, washed with dilute (1 + 9) hydrochloric acid and then with water until free from acid. The two crucibles were then dried and weighed as described above. As this two-crucible procedure permitted weighing immediately after removing the crucibles from the desiccator, the necessity for conditioning in the balance case was obviated thereby minimising errors due to the hygroscopic nature of the precipitate. The apparent molecular weights shown in Table I were determined by multiplying the precipitate weight, in mg, by ten.

TABLE I. APPARENT MOLECULAR WEIGHT OF THE PRECIPITATE

Test	Molecular weight found	Phosphorus found, *mg*	Error, *μg*
1	2214·0	3·100	+2
2	2212·0	3·097	−1
3	2214·1	3·100	+2
4	2212·0	3·097	−1
5	2213·6	3·099	+1
6	2211·5	3·096	−2
Mean	2212·9	3·098	
Theoretical	2212·87	3·098	

It is apparent that, under the conditions employed, the precipitate has the theoretical composition and that the theoretical factor of 0·01400 can be used for calculating the phosphorus content.

Effect of added sodium chloride and fluoride

As it was desired to use the gravimetric finish for analysis of organic materials after decomposition with sodium peroxide, the effect of adding 1·5 g of sodium chloride (equivalent to the 1 g of sodium peroxide used for the fusion) was investigated. Since fluorinated materials were to be analysed, the effect of added sodium fluoride ($\equiv$ 20 mg F^-), complexed with boric acid,[1] was also examined.

A slight amount of contamination was indicated but even in the worst case the error was not significant for semi-micro analysis of organic materials.

Analysis of organic materials

The results obtained for the analysis of organic materials are shown in Table II. The preliminary fusion and precipitation procedure previously described[1] was employed.

An additional filtration, before precipitation of the phosphorus, was necessary during the analysis of the silver salt because of the necessity for removing all the silver chloride. This is not necessary when the volumetric finish is used. The first three compounds listed in Table II are standard materials and the last four were produced during research work.

Alternative weighing procedures

(*a*) *After oven-drying:* The two-crucible technique has the disadvantage that, for routine work, a large number of crucibles and desiccators are necessary. It was found that the error caused by the slightly hygroscopic nature of the precipitate did not unduly influence the result when only the working crucible was dried at 160° and weighed against a tare kept in the balance case.

(*b*) *Rapid procedure:* The oven-drying procedures take over an hour from the completion of filtration. A rapid procedure was found by which this time could be cut to about 15 minutes, approximately the same time as is required for the volumetric finish.

After completion of the aqueous washing of the precipitate, the filter-crucible was removed and its exterior wiped to remove excess of water. The crucible was replaced in the suction apparatus and the interior washed with three 2 ml portions of dioxan and three 2 ml portions of dry ether. Dry air was drawn through the crucible for 5 minutes. It was then wiped, transferred to the balance pan and weighed on the fifth minute against a tare kept in the balance case. The empty filter crucible had been weighed initially after similar treatment.

TABLE II. ANALYSIS OF ORGANIC MATERIALS

Compound	Sample weight, *mg*	Phosphorus calc, *mg*	Phosphorus found, *mg*	Phosphorus calc, %	Phosphorus found, %	Absolute error, %
Triphenyl phosphine	25·27	2·98	2·95	11·81	11·68	−0·13
	25·17	2·97	2·94		11·67	−0·14
	28·19	3·33	3·29		11·68	−0·13
Tri-*m*-cresyl phosphate	24·09	2·03	2·01	8·41	8·36	−0·05
	22·71	1·91	1·90		8·38	−0·03
	24·61	2·07	2·06		8·37	−0·04
Tri-*n*-butyl phosphate	24·27	2·82	2·82	11·63	11·63	0
	24·38	2·84	2·83		11·60	−0·03
	24·76	2·88	2·87		11·60	−0·03
$C_6H_5{\cdot}O{\cdot}P(O)[O{\cdot}C_4H_9]_2$	24·57	2·66	2·65	10·82	10·80	−0·02
	30·98	3·35	3·34		10·79	−0·03
*$[CH_3{\cdot}O]_2P(O)C_6H_4{\cdot}NH_2$	19·45	3·00	2·97	15·40	15·28	−0·12
	18·82	2·90	2·86		15·17	−0·23
$[C_4H_9{\cdot}O]_2P(O)O{\cdot}Ag$	26·92	2·63	2·62	9·77	9·73	−0·04
	24·70	2·41	2·39		9·66	−0·11
$[C_3F_7{\cdot}CH_2{\cdot}O]_3PO$	54·47	2·62	2·62	4·81	4·81	0
	54·12	2·60	2·62		4·84	+0·03

* The preparation of this compound has not yet been described in the literature.

These precipitates were subsequently dried at 160° and weighed using the two-crucible technique in order to attempt to establish the composition of the solvent washed precipitate. The results obtained are shown in Table III.

TABLE III. RAPID DRYING PROCEDURE

Weight of precipitate, *mg*	225·28	225·29	225·14	225·08	225·28	225·16
Phosphorus found (factor 0·013757), *mg*	3·099	3·099	3·097	3·096	3·099	3·097
Phosphorus found (factor 0·013775), *mg*	3·103	3·103	3·101	3·100	3·103	3·102
Weight of precipitate after drying at 160°, *mg*	221·25	221·33	221·35	221·18	221·27	221·22
Phosphorus found, *mg*	3·098	3·099	3·099	3·097	3·098	3·097
Error, *μg*	0	+1	+1	−1	0	−1

The oven-drying check shows that there is no loss of precipitate by the use of the organic solvents. The factor 0·013757 was derived from the average weight of precipitate which gave an apparent molecular weight of 2252·05; 0·013775 is the theoretical factor for quinoline phosphomolybdate dihydrate (molecular weight 2248·90).

DISCUSSION

The results obtained by the two-crucible weighing technique indicate that, in spite of the hygroscopicity of the precipitate, very precise results may be obtained by using quinoline phosphomolybdate as a weighing form for the determination of phosphorus. It also appears that the theoretical factor can be used, although it was assumed that the potassium dihydrogen phosphate used to make the standard phosphate solution was pure. The fact that the results are so close to the theoretical indicates that this assumption was correct and it is considered that any other method of analysis to check the purity of the standard would be far less accurate than the method described.

For routine semi-micro determination of phosphorus, either of the alternative weighing procedures may be used. Of these, the rapid procedure seems to offer the greater advantage although the precipitate does not, under the conditions applied, have a stoicheiometric composition. It approximates closely to the dihydrate (*cf.* oxine phosphomolybdate[6]) and as can be seen in Table III, the theoretical factor for the dihydrate may be used to give results which are quite satisfactory for semi-micro analysis.

The two-crucible technique was used for the analysis of organic compounds and the results obtained were within the normally accepted limits. The preponderance of negative errors may be ascribed to slight impurity of the compounds or to losses during the procedure prior to precipitation. The reason for the consistently low results for the analysis of triphenyl phosphine is being investigated.

Although the method has been used only after mineralisation with sodium peroxide, it is considered that it should be equally satisfactory after decomposition by wet oxidation procedures or after the oxygen flask method.[7] The method has not been checked on the micro scale, the success of the semi-micro procedure being a good indication that Wilson's claim[2] for the utility of the gravimetric method for microanalysis is correct.

Acknowledgements—We thank Mr. E. J. P. Fear and Dr. I. M. White for provision of samples and Dr. R. Belcher for useful discussions.

Zusammenfassung—Nach Verschmelzung mit Natrium-hyperoxyd wird Phosphor in organischen Verbindungen durch eine Halb-mikrogravimetrische Methode bestimmt. Es wird gezeigt, dass der von 3 mg von Phosphor hergestellter Niederschlag von Chinolin-phosphormolybdänat die theoretische Zusammensetzung hat, und dass sehr präzise Resultate mittels einer besonderen Wägemethode erhalten werden. Zwei andere Wägemethoden werden beschrieben, die die Resultate fur Halbmikroarbeit befriedigend lieferten.

Résumé—Une fin gravimétrique à été appliquée à la détermination semi-micro du phosphore dans les composés organiques après fusion avec du peroxyde de sodium. On a montré que le précipité de phosphomolybdate de quinoléine, préparé à partir de 3 mg de phosphore, a la composition théorique et que, en utilisant une technique spéciale de pesée, on peut obtenir des résultats très précis. On décrit deux autres techniques de pesée qui donnent des résultats satisfaisants pour les travaux de semi-micro analyse.

REFERENCES

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DIRECT THERMOMETRIC TITRATION OF BORIC ACID

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Summary—Boric acid has been titrated directly with a standard solution of sodium hydroxide by the use of an automatic thermometric procedure. This titration was performed as one of a series of various types of titrations that could be made by an automatic thermometric procedure. Boric acid can be titrated either alone or in the presence of strong acids. Mannitol, if added to the solution of boric acid, sharpens the end-point by improving the shape of the titration curve; however, it is not necessary to add mannitol in order to obtain a good titration. Quantities of boric acid in the range of 0.3 meq. can be titrated by the automatic thermometric procedure with a relative standard deviation of 1%.

IT is customary in the determination of boron to acidify the solution that is obtained following its distillation as methyl borate, to titrate the acidified solution to the point of colour change of phenolphthalein, to add mannitol or glycerin, and then to titrate again to the phenolphthalein end point. The additional titer is taken as a measure of the boric acid that is present.

Hillebrand *et al.*[2] state: "An aqueous solution of boric acid cannot be titrated directly with a standard solution of sodium hydroxide, for no indicator is known that gives a sufficiently sharp colour change at the neutralization point, which occurs at approximately pH 11." The results that have been obtained in automatic thermometric titrations described herein indicate that boric acid can be titrated directly, either by itself or in the presence of a strong acid, with a standard solution of sodium hydroxide as the titrant.

The use of a thermometric procedure as an analytical tool dates back to Dutoit and Grobet.[1] Müller[6] suggested the use of a thermistor, a heat-sensitive device, as a replacement for the still-valuable Beckman thermometer. More recently Linde, Rogers, and Hume[4] published the results of their work on automatic thermometric titrations. Jordan and Alleman[3] have used a technique similar to that used by Linde, Rogers, and Hume to perform chelation titrations and to measure heats of chelation. Miller and Thomason[5] have used the thermometric titration as a means of determining free acid in the presence of certain hydrolyzable ions.

EXPERIMENTAL DETAILS

Apparatus

The equipment used in the titrations was very similar to that used by Linde, Rogers, and Hume[4] and by Jordan and Alleman.[3] The thermistor and bridge arrangement have been described by Jordan and Alleman.[3]

The stirring motor was a 115-v, a-c model, available from A. S. LaPine and Co. as Cat. Item No. 38286. The motor has two shafts, that is, an armature shaft turning at 1550 rpm and a slow speed

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* Operated for the U.S. Atomic Energy Commission by Union Carbide Nuclear Co., Division of Union Carbide and Carbon Corp.

shaft turning through an integral 5 : 1 geared speed reducer at 310 rpm. The motor was wrapped with a coil of 1/8 in.-dia. copper tubing through which water flowed at a slow rate. The cooling coil prevented an excessive rise in the temperature of the motor during long periods of operation. A glass stirrer was made by twisting a piece of flat glass into a spiral that was 1½ in. long and ½ in. wide and attaching it to a ¼-in. dia. glass rod.

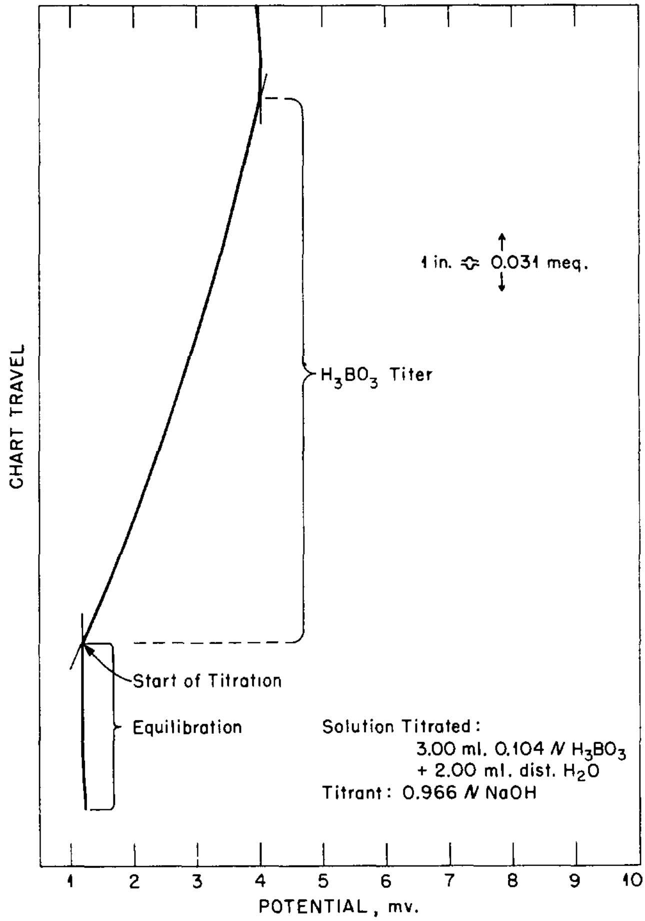

FIG. 1. Typical curve for the thermometric titration of boric acid with sodium hydroxide solution.

A Brown Electronik recorder, model No. Y153X17(VA)-X-30A3C2G, made by the Brown Instruments Division of the Minneapolis-Honeywell Regulator Co., Philadelphia, Pa., was used to record the potential across the bridge. This model recorder is convenient to use in experimental work since it has a variable span and variable zero suppression.

A Greiner, syringe-type microburette, which has a delivery capacity of 1 ml, was used in the investigation. It was fitted with a constant-speed, Bodine motor through a coupling gear so that delivery of titrant would be at a rate constant with time. A release mechanism makes possible the rapid refilling of the burette by manually turning a crank.

The titration was performed in a 20-ml, polyethylene beaker that was supported on a Styrofoam block; both the beaker and the support were contained in a 250-ml, wide-mouth, Dewar flask.

Reagents

The solutions of boric acid were made up by weighing out reagent-grade, crystalline boric acid and dissolving it in water. Solutions of sulphuric acid and of hydrochloric acid were made by diluting reagent-grade acids.

Procedure

The test portion of a solution was pipetted into the polyethylene beaker. Sufficient distilled water was added to bring the total volume to 5.00 ml. The stirring motor, the thermistor bridge, and the recorder were turned on. The recorder was standarised, and the bridge was brought to a balance point. After a 5- to 10-minute equilibration period, the bridge was rebalanced, and the drive motor of the burette was turned on. The titration curve was recorded and the equipment shut down. The burette was refilled with the standard solution of sodium hydroxide, and the equipment was then ready for another titration.

A calibration factor was established to relate inches of chart travel to milliequivalents of sodium hydroxide delivered by the burette; this was done by titrating aliquots of a standard solution of hydrochloric acid with a standard solution of sodium hydroxide.

TABLE I. LINEARITY TEST DATA

Solution Titrated: indicated test portion of 0.104*N* H_3BO_3 + dist. H_2O to make a total of 5.00 ml.

Titrant: 0.966*N* NaOH

Calibration Factor: 1.0 in. of chart travel $\approx$ 0.031 meq. H_3BO_3

Test Portion of 0.104*N* Soln., *ml*	*meq*	Chart Travel, *in.*	NaOH, *meq*
1.00	0.104	3.10	0.097
2.00	0.208	6.25	0.196
3.00	0.312	9.40	0.294
4.00	0.416	12.60	0.394
5.00	0.520	15.60	0.488

RESULTS AND DISCUSSION

A series of titrations were performed to determine the feasibility of the thermometric titration of boric acid. Boric acid was titrated with sodium hydroxide solution both by itself and in the separate presence of mannitol, hydrochloric acid, and sulphuric acid. The results obtained with hydrochloric acid were so similar to those obtained with sulphuric acid that an extended series of titrations were made with only sulphuric acid. The addition of mannitol to the boric acid solution improves the shape of the titration curve; the starting point and the end-point are more distinct. The curve closely resembles the curve obtained in the titration of strong acids with sodium hydroxide solution. In a solution that contains both boric acid and sulphuric or hydrochloric acid, the strong acid is titrated first and then the boric acid is titrated.

The linearity of the results of the titration of boric acid with a standard solution of sodium hydroxide is illustrated by the data of Table I. A typical titration curve is shown in Figure 1. It is shown in Figure 2 how the addition of mannitol to the boric acid solution that is being titrated improves the shape of the curve.

The results obtained in the sequential titrations of constant amounts of boric acid and variable quantities of sulphuric acid in the presence of each other are given in Table II. The curve that results from the sequential titrations of these acids is shown in Figure 3.

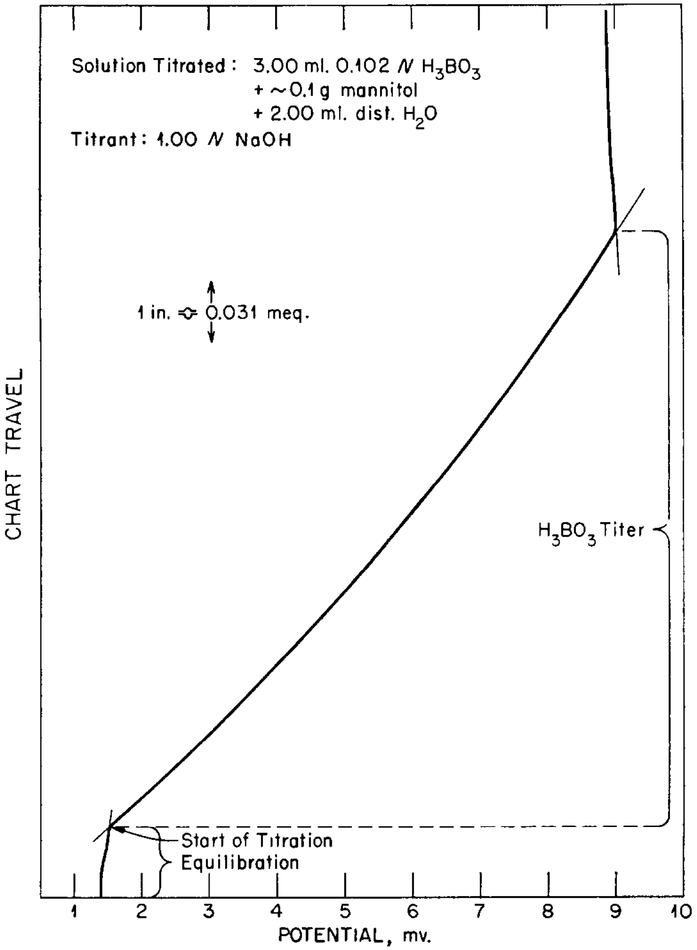

FIG. 2. Typical curve for the thermometric titration of boric acid with sodium hydroxide solution in the presence of mannitol.

TABLE II. SEQUENTIAL TITRATION OF SULPHURIC ACID AND BORIC ACID (CONSTANT AMOUNT OF BORIC ACID)

Solution Titrated: 1.00 ml of 0.102*N* H_3BO_3 + indicated test portion of 0.908*N* H_2SO_4 + dist. H_2O to make 5.00 ml.

Titrant: 1.000*N* NaOH

Calibration Factor: 1.0 in. of chart travel ≎ 0.031 meq.

Test Portion of 0.908*N* H_2SO_4, *ml*	NaOH Required, *meq*	
	H_2SO_4 Titer	H_3BO_3 Titer
—	—	0.098
0.05	0.039	0.101
0.10	0.089	0.102
0.20	0.178	0.103
0.50	0.461	0.103

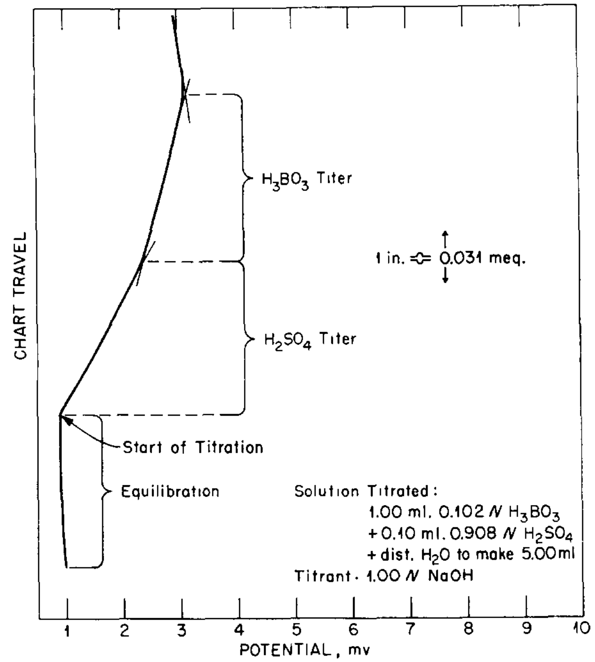

FIG. 3. Typical curve for the sequential thermometric titration of sulphuric acid and boric acid.

The results obtained in the sequential titrations of constant amounts of sulphuric acid and variable quantities of boric acid in the presence of each other are given in Table III.

The results of a study of the precision of the method indicate that in ten replicate titrations of 3 ml of 0.102*N* H_3BO_3 with 1.000N NaOH a standard deviation of 1.19% was obtained.

The data presented demonstrate that boric acid can be titrated directly with a standard solution of sodium hydroxide by thermometric means. The boric acid can

TABLE III. SEQUENTIAL TITRATION OF SULPHURIC ACID AND BORIC ACID (CONSTANT AMOUNT OF SULPHURIC ACID)

Solution Titrated: 0.10 ml of 0.908*N* H_2SO_4 + indicated test portion of 0.102*N* H_3BO_3 + dist. H_2O to make 5.00 ml.

Titrant: 1.000*N* NaOH

Calibration Factor: 1.0 in. of chart travel ≙ 0.031 meq.

Test Portion of 0.102*N* H_3BO_3, *ml.*	NaOH Required, *meq.*	
	H_2SO_4 Titer	H_3BO_3 Titer
1.00	—	0.098
—	0.091	—
1.00	0.088	0.103
2.00	0.090	0.200
3.00	0.086	0.306
4.00	0.102	0.408
5.00	0.097	0.466

be determined in the presence of a strong acid, and the quantity of strong acid present can also be determined. The addition of mannitol to the boric acid solution improves the titration, but is not a requisite.

Acknowledgement—The authors are indebted to M. T. Kelley for his invaluable advice and to Harold C. Jones for the attachment of motor and gear system to the Greiner microburette.

Zusammenfassung—Borax-säure wird mit einer Standard-Lösung von Natrium-hydroxyd mittels eines automatischen thermometrischen Verfahrens direkt titriert. Man kann Borax-säure entweder allein oder in der Anwesenheit von starken Säuren titrieren. Wenn Mannit der Borax-säure-lösung hinzufügt wird, so wird der End-punkt durch Verbesserung der Form der Titrationskurve geschärft. Es ist jedenfalls nicht nötig, Mannit hinzufügen, um eine gute Titration zu erhalten. Borax säuremengen auf dem Gebiet von 0.3 milliäquivalent kann man durch das automatische thermometrische Verfahren mit einer relativen Standard-Abweichung von 1% titrieren.

Résumé—L'acide borique a été titré directement avec une solution étalon de soude en utilisant une technique thermométrique automatique. Le titrage était effectué comme l'un d'une série de types variés de titrages qui peuvent être faits par un tel procédé. On peut titrer l'acide borique soit seul, soit en présence d'acides forts. Le mannitol ajouté à la solution d'acide borique rend plus net le point équivalent en améliorant la forme de la courbe de titrage; cependant il n'est pas nécessaire d'ajouter du mannitol pour obtenir un bon titrage. On peut titrer des quantités d'acide borique de l'ordre de 0,3 milliéquivalents par ce procédé automatique thermométrique avec une déviation relative standard de 1%.

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ACTIVATION ANALYSIS OF TUNGSTEN IN HIGH ALLOY STEELS

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Summary—Tungsten was determined by neutron activation analysis in high alloy steels. As the absorption cross-section of high alloy steels can be quite high, precautions are necessary to avoid errors due to self-shielding effects, if irradiated samples are large. Two procedures were developed namely with and without chemical separation of tungsten. Although the latter procedure is reliable in the absence of specified limiting amounts of Cu, As and Mo results are available only after 15 days. This disadvantage can be avoided by separating tungsten as tungstic acid. Both procedures were tested successfully on a number of N.B.S. standard steels. Accuracy and precision appear to be of the same order of magnitude as careful chemical analysis.

INTRODUCTION

WHEN determining tungsten in high alloy steels it is difficult to achieve quantitative separation of small amounts of tungstic acid, when cinchonine or β-naphthoquinoline are used as precipitants. Furthermore, the precipitate is impure due to co-precipitation or adsorption of molybdenum, vanadium, tantalum, niobium, silica and other elements.

It is possible to avoid these difficulties when determining tungsten by neutron activation analysis, as the nuclear properties of this element are rather favourable. Although activation analysis is usually only used for the determination of trace elements, it appears that the method is also valuable for the analysis of minor constituents in complex materials, as shown previously in the activation analysis of vanadium in high alloy steels containing from 0·01 to 2% of this element.[1]

NUCLEAR DATA

Natural tungsten consists of a number of isotopes which give rise to several radioactive species, whose properties are summarised in Table I.

TABLE I. PROPERTIES OF TUNGSTEN ISOTOPES

Natural isotope	Abundance, θ	$\theta \cdot \sigma_{act}$, *barns*	Radioisotope formed	$T_{\frac{1}{2}}$	Radiation and energy, *MeV*
^{180}W	0·0014	0·028	^{181}W	140 d	E.C.//γ0·136/0·152
^{182}W	0·262	—	^{183}W	stable	—
^{183}W	0·143	—	^{184}W	stable	—
^{184}W	0·307	0·61	^{185}W	74 d	β^- 0·426/0·368//γ 0·058
^{186}W	0·284	9·7	^{187}W	24 h	β^- 0·408/0·627/1·318 γ 0·68/0·645/0·478 0·133/0·072

As can be seen from Table I, the predominantly formed isotope is ^{187}W, half life 24.0 h, whose decay scheme is given in Fig. 1.

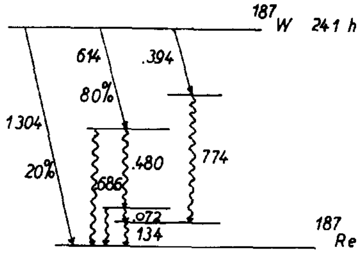

FIG. 1. Decay scheme of ^{187}W(3).

INTERFERING ACTIVITIES

When irradiating high alloy steels, several isotopes are produced from the steel constituents. The most important ones are represented in Table II.

TABLE II. PROPERTIES OF STEEL CONSTITUENTS, SUBJECT TO ACTIVATION BY THERMAL NEUTRONS

Element	% in steel	Natural isotope	$\theta . \sigma_{act}$	Isotope produced	$T_{\frac{1}{2}}$	Radiation and energy
V	$\leqslant 2·5$	V^{51}	4·5	V^{52}	3·75 m	β^- 2·7// γ . 1·46
Cu	0·1	Cu^{65}	0·68	Cu^{66}	5·1 m	β^- 2·63/1·59// γ 1·04
Co	up to 45	Co^{59}	17	Co^{60m}	10·5 m	γ 0·058
Mo	seldom >2	Mo^{100}	0·019	Mo^{101}	14·6 m	β^- 2·2/1·2// γ 0·96/0·191
Mn	0·25–1·3	Mn^{55}	13	Mn^{56}	2·56 h	β^- 2·86/1·05/0·75// γ 1·77/0·82/2·06
Ni	up to 40	Ni^{64}	0·03	Ni^{65}	2·59 h	β^- 2·09// γ 1·49/1·12
Cu	0·1	Cu^{63}	2·97	Cu^{64}	12·9 h	E.C./β^+/β^-// γ 1·34
As	0·07	As^{75}	4·3	As^{76}	26·4 h	β^- 0·4–2·98// γ 0·55/0·64/1·2/1·4/1·7/2·05
Mo	seldom >2	Mo^{98}	0·03	Mo^{99}	68 h	β^- 1·23/0·45/0·2// γ 0·74/0·18/0,14 /0·78/0·367
Cr	up to 20	Cr^{50}	0·73	Cr^{51}	27 d	E.C.// γ 0·32
Fe	chief const.	Fe^{58}	0·0026	Fe^{59}	45 d	β^- 0·26/0·46// γ 1·28/1·1/0·19
Ta	1.2	Ta^{181}	21	Ta^{182}	118 d	β^- 0·53/1·1// γ 0·05–1·2
Co	up to 45	Co^{59}	34	Co^{60}	5·2 y	β^- 0·309/1·48// γ 1·17/1·33

If tungsten is not chemically separated before the activity measurements, a number of these isotopes are likely to interfere. Whereas ^{52}V, ^{66}Cu, ^{60m}Co and ^{101}Mo will decay completely within a few hours after the end of the bombardment, ^{56}Mn is still measurable after 24 h. Analysis of the decay curve allows us to correct for this activity as the half-life is sufficiently different from that of ^{187}W. Activities due to the long lived species ^{51}Cr, ^{59}Fe, ^{182}Ta and ^{60}Co can also be easily distinguished from ^{187}W by analysis of the decay curve. The half lives of ^{64}Cu, ^{76}As and ^{99}Mo are however similar to that of ^{187}W and are likely to cause serious interference if present in large amounts. Interferences as a function of time are represented in Fig. 2 for ^{64}Cu, ^{76}As and ^{99}Mo to ^{187}W ratios of respectively 0.2, 0.01 and 5. Measurements were carried out with a Tracerlab P-20A well-type γ-detector after an activation run of 1 hour at a flux of approximately 10^7 n/cm^2 sec. It is apparent that chemical separation will be necessary if these elements are present in larger amounts than those indicated above, although this will only occur exceptionally.

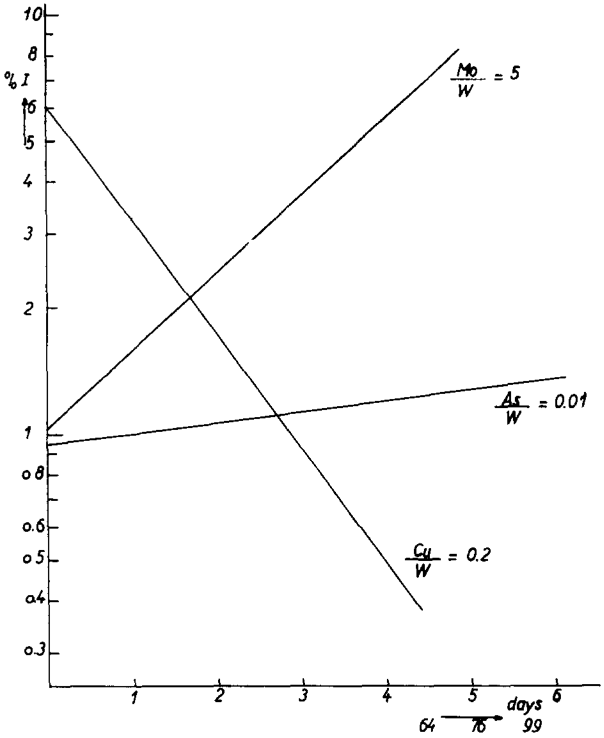

FIG. 2. Interfering activities of ^{64}Cu, ^{76}As, ^{99}Mo.

NEUTRON SELF-SHIELDING EFFECTS

As the cross-sections of the WO_3 used as reference standard and of some high alloy steel constituents are quite large, errors due to self-shielding effects are to be expected, especially when large samples are required as is the case at a flux of approximately 10^7 n/cm^2 sec, available at the Louvain cyclotron. Fig. 3 gives a survey of the

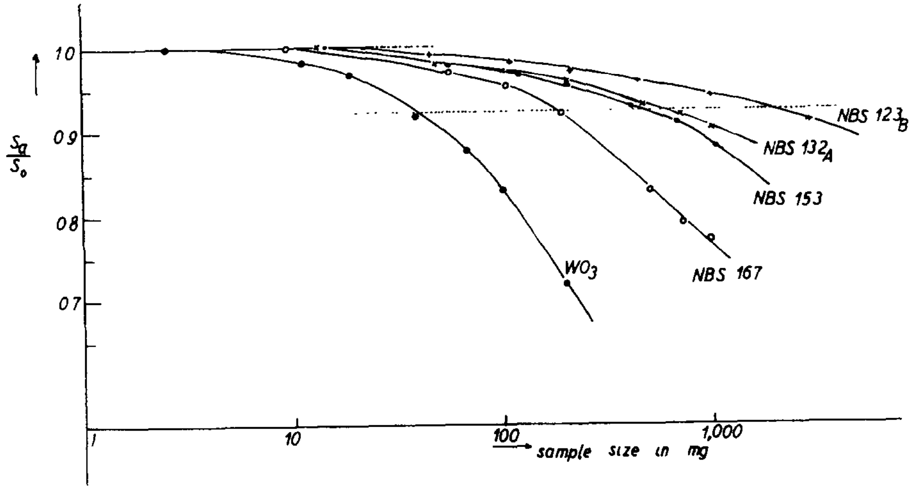

FIG. 3. Influence of sample size on the neutron self shielding.

influence of sample size on the specific activity of WO_3 and of the different steels under investigation.

As is apparent from Fig. 3, neutron self-shielding effects are quite important for WO_3 and steel NBS 167. These results are in agreement with the computed average absorption cross-section of the steel samples summarised in Table III.

TABLE III. MEAN NEUTRON ABSORPTION CROSS-SECTIONS AND COMPOSITION OF NBS HIGH ALLOY W STEELS

% i	% Fe	% Mn	% Ni	% Cr	% Co	% V	% Mo	% W	% Ta	$\frac{\sigma_i . \% i}{100}$
σ_i	2·4	13·3	4·6	3·1	37	2·5	4·9	18	22	
NBS steel										
132_A	81·0	0·268	0·137	4·21	—	1·94	4·51	6·20	—	3·5
153	73·9	0·219	0·107	4·14	8·45	2·04	8·39	1·58	—	5·4
155	96·6	1·24	0·100	0·485	—	0·014	0·039	0·517	—	2·6
123_B	98·1	—	—	—	—	0·05	0·17	0·18	0·20	$2{\cdot}4^5$
167	2·13	1·64	20·65	20·00	42·9	0·01	3·90	4·5	0·08	17·4

Three methods have been used, in order to avoid errors, due to self-shielding: at a high neutron flux of 10^{11} n/cm^2 sec, as available in the BR1 reactor, a sufficiently small sample size could be taken, so as to make self shielding effects negligible. When using a flux of 10^7 n/cm^2 sec however, the sample size of the WO_3 reference standard and of the steel samples were adjusted to obtain a constant effect at a level illustrated in Fig. 3 (dotted line). In some other analyses errors due to self shielding were avoided by using an internal standard. This procedure has been described in detail elsewhere.[1,2]

TUNGSTEN DETERMINATION WITHOUT CHEMICAL SEPARATION

As shown above, the activity due to ^{187}W in the presence of other species, activated in high alloy steels, can be computed from the graphical analysis of the decay curve if Cu, As and Mo do not exceed certain limits, as is the case with the investigated NBS steels.

Procedure

Appropriate amounts of steel turnings and of WO_3 are weighed in polythene containers. When using the cyclotron as a neutron source, by 11·5 MeV deuteron bombardment on a beryllium target, sample size was adjusted so as to obtain a constant self-shielding effect.

At a 100 μA beam intensity, a neutron flux of approximately 10^7 n/cm^2 sec was obtained in the paraffin block, used as moderator. This cylindrical block, provided with concentric irradiation holes, rotated near the cyclotron at 20 rpm. In these conditions an irradiation time of 1 hour gives an activity, large enough to allow accurate counting.

In the BRI reactor a flux of 10^{11} n/cm^2 sec was available, so that samples small enough to avoid self shielding were possible. An irradiation time of about 1 minute is convenient.

Activity measurements were carried out twice daily during 15 days by means of a Tracerlab P-20A well type Na(T1)I detector, coupled to a Tracerlab Superscaler. The sensitivity of the preamplifier was regulated so as to discriminate against weak gamma radiation to avoid self absorption effects.

A typical decay curve for steel 132_A and 123_B is represented in Fig. 4, and results are summarised in Table IV.

From Table IV it appears that the results are in good agreement with those of the NBS, the mean error on a number of determinations being of the same order of magnitude as those computed from the NBS certificates.

For steel samples 167 and 123B the internal standard method was also applied, allowing a direct correction of neutron self-shielding effects and possible neutron flux irregularities. In this case two steel samples were irradiated of respectively a and b mg, c mg pure WO_3 being homogeneously mixed with the latter. If A_{tL} and A'_{tL} are the respective activities of the long lived species at a time t after decay of ^{187}W, the neutron correction factor will be given by

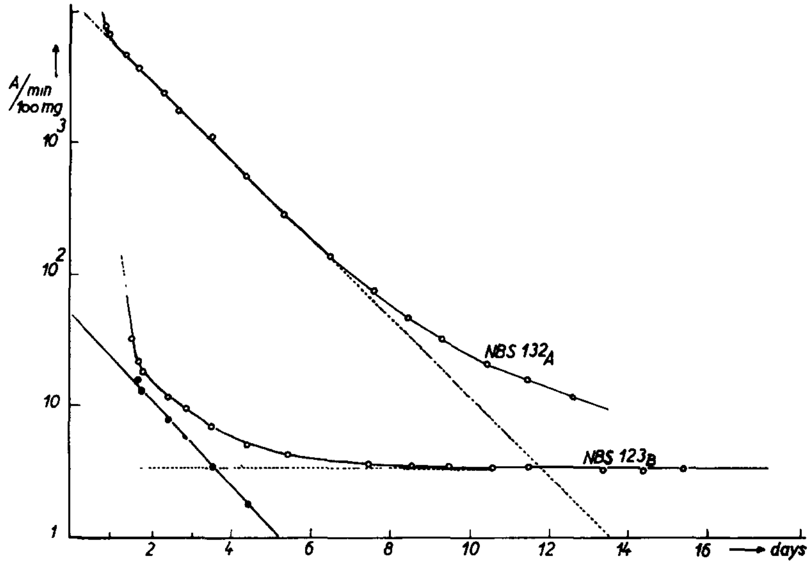

FIG. 4. Decay of activated steel samples (cyclotron irradiation).

$$\frac{A_{tL}}{A'_{tL}} = \frac{a}{b} \cdot \alpha$$

If $A_{t_0,w}$ and $A'_{t_0,w}$ are the computed tungsten activities at the time t_0, the specific activity in counts per mg of ^{187}W in the sample at this moment will be given by

$$S_{t_0,w} = \frac{1}{c}\left[A'_{t_0,w} \cdot \alpha - \frac{b}{a} \cdot A_{t_0,w}\right]$$

The tungsten content in per cent is then given by

$$\%W = \frac{A_{t_0,w} \cdot 100}{a \cdot S_{t_0,w}}$$

Decay curves corresponding to an analysis of steel 123B are represented in Fig. 5. Results are summarised in Table V and appear to be in good agreement with those of the NBS.

Table IV. Activation analysis for W without chemical separation

NBS Steel	NBS results	Mean error, $\bar{\Delta}$	Sample size, *mg*	% W	Mean value	Mean error, $\bar{\Delta}$
132$_{\mathrm{A}}$	6·20	0·07	510·9 506·4 601·9 601·2 603·4 614·6	6·07 6·13 6·15 6·05 6·21 6·25	6·14*	0·08
			22·272 22·484 18·363 17·748	6·24 6·25 6·20 6·11	6·20†	0·045
167	4·5	provis. certif.	190·0 190·0	4·25 4·30	4·30*	0·05
			11·082 14·174 13·230 20·284	4·39 4·41 4·42 4·37	4·40†	0·02
153	1·58	0·027	506·4 501·2	1·58 1·59	1·59*	0·01
			17·672 32·379 23·084 28·259	1·61 1·56 $1{\cdot}60_5$ 1·62	1·60†	0·02
155	0·517	0·006	1,055·9 1,092·9	0·516 0·512	0·514*	0·01
			66·851 68·547 34·519	0·527 0·528 0·508 0·518	0·520†	0·007
123$_{\mathrm{B}}$	0·18	provis. certif.	2,122·0 2,009·6	0·191 0·209	0·20*	0·02

* Cyclotron activation

† BR1 reaction activation

TUNGSTEN DETERMINATION WITH CHEMICAL SEPARATION

As pointed out before, chemical separation of tungsten becomes necessary as soon as the Cu, As and Mo to W ratios are higher than the respective values of 0·2, 0·01 and 5. Furthermore, results from the direct method do not become available until 15 days after the irradiation, as graphical analysis of the decay curves are necessary. It is possible to avoid these disadvantages by chemical separation of tungsten as tungstic acid.

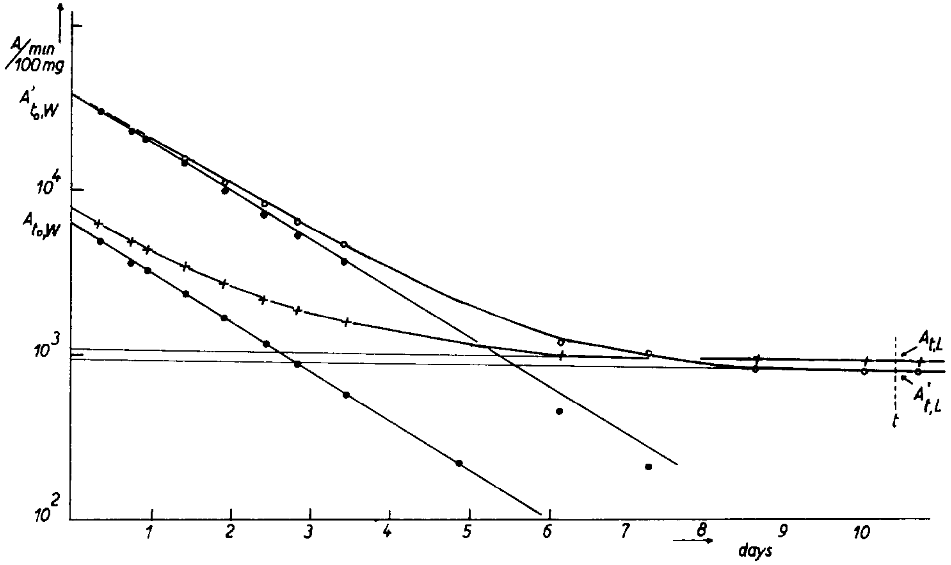

FIG. 5. Determination in NBS steel 123B by means of internal standard.

Procedure

The irradiated steel samples are dissolved in 6 *N* HCl. After the reaction has subsided, concentrated HNO_3 is added dropwise, followed by 20 ml $HClO_4$ (d = 1·67). The solution, containing the yellow tungstic acid precipitate is heated on a hot plate until HCl and HNO_3 are completely removed. After cooling, the solution is diluted with 50 ml water and 2 to 5 ml H_2O_2 (30%) are added to solubilize the tungstic acid as peroxytungstate. 3 ml 1% tungsten carrier (as $Na_2WO_4.2H_2O$) and 5 ml 1% vanadium (as Na_3VO_4) are added. The latter reduces molybdate adsorption on the tungstic acid precipitate to a considerable extent, as shown experimentally in separate tracer experiments.

The solution is heated on a hot plate, causing homogeneous precipitation of the tungstic acid by

TABLE V. ACTIVATION ANALYSIS WITH INTERNAL STANDARD

NBS steel	NBS results	Means error, $\bar{\Delta}$	Sample size, *mg*			α	$A_{0,W}$	$A'_{0,W}$	% W	Mean	$\bar{\Delta}$
			a	*b*	*c*						
167	4·5	provis. certif.	397·7 497·8 610·6 682·4 499·8	381·5 406·5 451·6 698·2 508·8	126·6 136·2 126·7 142·1 127·6	0·997 0·874 1·112 1·003 0·775	6,980 7,105 9,650 10,380 12,150	53,420 52,240 49,660 62,370 61,820	4·77 4·88 4·35 4·16 4·50	4·53*	0·23
			23·672 27·736 20·558	30·297 29·537 40·090	7·457 8·753 12·322	0·983 0·991 1·006	29,500 29,400 28,600	57,000 63,500 88,250	4·67 4·74 4·56	4·66†	0·06
123B	0,18	provis. certif.	1061·1 770·8 821·9	922·7 917·6 951·3	9·523 17·270 10·835	0·99 1·076 0·976	506 325 172	2,980 3,810 1,580	0·181 0·196 0·169	0·18[a]†	0·007

* Cyclotron activation
† BR1 reactor activation

decomposition of the peroxyacid. Disappearance of the wine red colour of peroxyvanadic acid serves as an indicator. Heating is continued for an additional 15 minutes, the precipitate filtered off on fine grained paper and washed with 3% HNO_3.

Tungstic acid adhering to the beaker wall is dissolved in a few drops 5% NaOH and 30% H_2O_2. The filtrate is transferred to this original beaker and the precipitation repeated after addition of a second 3 ml portion of tungsten carrier.

This procedure ensures a tungsten recovery better than 99·8%. The tungstic acid precipitates, together with the filter paper, are counted either separately or together in the counting equipment described above.

This procedure gives a sufficient radiochemical purification from most of the steel constituents as shown by decay measurements, gamma spectrometry and measurement of relative beta absorption according to Plumb and Lewis.[4]

In the presence of tantalum, this element is coprecipitated with tungsten and necessitates a graphical analysis of the decay curve. The presence of niobium or titanium causes no radiochemical interference.

Results are summarized in Table VI and appear to be in good agreement with the expected values.

TABLE VI. ACTIVATION ANALYSIS FOR W, WITH CHEMICAL SEPARATION

NBS steel	NBS results	Mean error, $\bar{\Delta}$	Sample size, *mg*	% W	Mean value, *m*	Mean error, $\bar{\Delta}$
132_A	6·20	0·07	491·4 507·0 596·7 598·5	6·17 6·28 6·25 6·22	6·23*	0·04
155	0·517	0·006	4008·1 1067·6	$0{\cdot}52_1$ $0{\cdot}52_3$	$0{\cdot}52^2$*	0·001
167	4·5	provis. certif.	190·5 190·0	4·17 4·25	4·21*	0·04
			5·075 5·382 9·816	4·30 4·26 4·35	4·30†	0·03
153	1·58	0·027	467·6 518·1	1·60 1·60	1·60*	0·01
123_B	0·18	provis. certif.	1967·8 2085·5	0·170 0·172	0·171*	0·001

* Cyclotron irradation
† BR1 reactor irradiation

Acknowledgments—Acknowledgments are due to the staff members of the cyclotron in Louvain and particularly to Dr. Képenne, as well as to Dr. de Dorlodot of the S. C. K. in Mol.

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Zusammenfassung—Wolfram wird durch Neutron-Aktivierungsanalyse in Hochlegierungsstahlen bestimmt. Da der Absorbierungsquerschnitt der Hochlegierungsstahlen gelegentlich ziemlich gross ist, sind Vorsichtsmassregeln nötig, um Fehler von selbstschirmenden Effekten zu vermeiden, wenn die gestrahlten Proben gross sind.

Zwei Verfahren, mit und ohne chemische Trennung von Wolfram, werden entwickelt. Obgleich das Verfahren zuverlässig ist, sind Resultate erst nach 15 Tagen vorhanden. Man kann diesen Nachteil durch Trennung von Wolfram als Wolframsäure vermeiden. Beide Verfahren werden mit einigen NBS Standard-Stahlen probiert. Genauigkeit und Präzision scheinen genau so gross zu sein wie bei sorgefältiger chemische Analyse.

Résumé—On a mis au point une méthode d'analyse par activation d'aciers hautement alliés à l'aide de neutrons thermiques. La section efficace de certains aciers étant assez grande, certaines précautions sont nécessaires afin d'éviter des effects de "self-shielding", surtout si les échantillons à irradier sont grands. Deux modes opératoires ont été développés: avec et sans séparation chimique.

Les résultats obtenus à l'aide des deux procédés sont valables, quoique dans le dernier cas ils ne sont disponibles qu'après 15 jours. Les deux méthodes ont été appliquées à un nombre d'aciers du N. B. S.

La précision et la reproductibilité sont du même ordre de grandeur que l'analyse chimique.

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THE USE OF EDTA TO ELIMINATE INTERFERENCES IN THE ZINC-FERROCYANIDE TITRATION

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Summary—The use of EDTA as a masking agent in the titration of zinc with potassium ferrocyanide has been investigated. If the pH is controlled at 2.0 to 2.1 and EDTA is added, accurate determination of zinc can be made in the presence of iron, nickel, lead and aluminium. However, the interference of copper, cobalt, cadmium and manganese could not be eliminated by this method.

THE determination of zinc by titration with standard potassium ferrocyanide solution has been extensively studied.[6] Lingane and Hartley[7] have noted the profound effect of pH on the composition of the zinc-ferrocyanide precipitate and other characteristics of the titration. Although they obtained accurate results over a pH range of 1 to 3, only samples of pure zinc were titrated. Because many metal ions form precipitates with ferrocyanide, its analytical usefulness is rather limited. This work was undertaken to make the ferrocyanide titration more generally useful in the presence of interfering metal ions. Cheng[3] has investigated the use of strong complexing agents, such as EDTA, for the elimination of interferences in the titration of manganese with ferrocyanide, Cheng was not able to determine zinc by the titration of ferrocyanide in the presence of EDTA at pH 2.5. In the present study a method has been developed for the titration of zinc in the presence of various metal ions whose interferences are eliminated by complexing them with EDTA. Optimum pH values have been established and various electrical methods of end-point detection have been discussed.

REAGENTS AND APPARATUS

CP chemicals and distilled water were used to prepare all reagent solutions. The standard zinc solution was made by dissolving pure zinc in 1 : 1 hydrochloric or sulphuric acid with the appropriate amount of water.

A manual polarograph was used as an end-point detecting device in all the amperometric titrations. The electrodes used for two-electrode amperometry were prepared by sealing pieces of platinum wire in soft glass tubing. For one-electrode amperometry a Sargent Syncronous Rotator and a hook-type electrode (E. H. Sargent and Co., Chicago, Illinois) were used.

Potentiometric titrations at constant current were performed using the same electrode systems as used for two-electrode amperometry. The constant current was maintained by an apparatus similar to that of Bishop.[1] In this case, potentials were measured with a Leeds Northrup Student-type potentiometer.

DISCUSSION

End-point detection

Various electrical end-point detection methods for the titration of zinc with ferrocyanide have been proposed.[2,5,7,9] Of these, it was found that amperometric methods lead to easier and more accurate end-point detection. In general, the potentiometric methods were found to be somewhat slow in attaining stable potentials. This was especially true of classical potentiometry, but even true of potentiometric titrations at constant current using two indicator electrodes. Of the two amperometric methods, amperometry using two indicator electrodes has the advantage of simplicity since no reference electrode is necessary. However, greater sensitivity was found in the use of one-electrode amperometry. This is undoubtedly due to the fact that the indicator electrode is rotated and thus more effective stirring is achieved. One-electrode amperometry also has the advantage that no ferricyanide ion need be added as in the other end-point detecting methods. In this study two-electrode amperometry was generally used because of its simplicity except in those cases where the addition of ferricyanide was impossible due to side reactions, such as in the attempted determination of zinc-copper mixtures. A brief study indicated that a potential of 0·1 volt applied across the two indicator electrodes yielded satisfactory results when approximately ten drops of a 1% potassium ferricyanide solution (freshly prepared) were added per 100 ml of solution. The form of the titration curve has been discussed by Kies.[5] Ordinarily the curve need not be plotted as the end-point can easily be determined. Ideal curves were generally not obtained, but the end-point was always marked by a sharp increase in current when one drop of excess 0·1 *N* ferrocyanide solution was added. In some cases, a distinct dip in the indicator current was noticed just prior to the end point.

Effect of pH *and* EDTA *concentration*

The effect of EDTA on the results of the zinc-ferrocyanide titration was studied at varying pH. The range of possible usefulness was between pH 1 and 3. Outside this range the composition of the zinc ferrocyanide precipitate tends to vary and useful results are not obtained. Ideally, a pH close to 3 would allow the optimum possibility for elimination of interferences. However, it was found that unless the pH was 2.1 or lower, the presence of EDTA would cause errors in the determination of zinc. This explains the difficulty Cheng[3] had, since his attempted titrations were performed from pH 2.3 to 2.5. Even at a pH of 2.1, only a certain concentration of EDTA could be tolerated before noticeable complexation of the zinc occurred. As indicated in Table I, the ratio of moles of excess EDTA per mole of zinc can be no higher than about 0.6. This, however, would allow reasonable leeway, especially in the determination of those samples whose approximate composition is known. It was found later that sufficient EDTA could be added to a sample solution to complex all of some interfering ions, such as nickel, and then the excess of 0.6 moles, with no ill effect.

The elimination of interferences

The effectiveness of the masking power of EDTA on various interfering metals was tested by titrating synthetic mixtures containing zinc ion and various other metal ions. To an aliquot of zinc solution containing approximately 150 mg of zinc were added varying amounts of the metal ion whose interference was to be tested. The amounts of the various metals taken do not necessarily represent the maximum possible concentration, but were chosen on the basis of normal analytical situations. Sufficient 0.1 *M* solution of the tetra-sodium salt of EDTA was added to complex all of the interfering metal ion and an excess equivalent to approximately half of the zinc. The pH was adjusted to 2.1 ± 0.05 and ten drops of potassium ferricyanide solution were added. The solution was diluted to approximately 100 ml with water and titrated amperometrically with 0.1 *M* potassium ferrocyanide solution. Since a pH greater than 2.1 is generally assured by using the tetra-sodium salt of EDTA, the pH may easily be adjusted to 2.1 with dilute hydrochloric acid. The pH remained constant throughout the titration. Efficient stirring was provided by a magnetic stirrer.

TABLE I.

Moles EDTA/Mole Zn	Zinc, *mg*		Error, %
	Taken	Found	
0	149.8	150.2	+0.3
0.4		149.5	−0.2
0.4		150.2	+0.3
0.6		149.4	−0.3
0.6		153.3	+2.3
0.75		143.2	−4.4
0.75		140.2	−6.4
1.00		121.2	−19.1

The interference of nickel, iron, and lead were successfully eliminated by this method as indicated in Table II. In addition, it was found that aluminium, manganese, chloride and sulphate ions caused no errors in the titration of zinc whether or not EDTA was present. The interferences of copper, cadmium, and cobalt could not be eliminated by the addition of EDTA. This is what might be expected since the EDTA complexes of lead, nickel, and iron are stronger than that of zinc, but those of cadmium and cobalt are of equal strength.[8]

TABLE II.

Metals added, *mg*		Zinc, *mg*		Error, %
		Taken	Found	
Fe^{III}	28	163.4	163.4	0.0
	55		161.9	−0.9
	83		161.9	−0.9
Ni^{II}	24	163.4	163.4	0.0
	48		163.4	0.0
	72		158.9	+2.7
Pb^{II}	104	170.3	169.8	−0.3
	208		169.8	−0.3
	312		170.8	+0.3
Al^{III}*	23	170.3	170.1	−0.1
Mg^{II}*	34	170.3	170.7	+0.2

* No EDTA added.

A special effort was made to eliminate interferences of copper since copper–zinc alloys are of great commerical importance, and since the strength of the copper EDTA complex indicated that this might be possible. Copper has been effectively masked with thiosulphate ion in certain compleximetric titrations.[4] In the ferrocyanide titration, however, since the pH had to be maintained at a low value, thiosulphate ion decomposed rather rapidly and, although some success was achieved, erratic results were generally found. The addition of hydrazine sulphate was also tried as a method of eliminating the interference of copper. It was found that the hydrazine sulphate reduced the copper to cuprous ions which would not react with ferrocyanide. Complete reduction was achieved by removing the air from the solution to be titrated with purified nitrogen and the addition of 25 ml of saturated hydrazine sulphate solution. After the pH was adjusted to 2.1, the zinc was titrated using one-electrode amperometry as an end-point detecting device. An indicator electrode potential of +0.25 volt *vs.* S.C.E. was selected. Current–potential curves indicated that this potential would provide a maximum current from excess ferrocyanide ion with a minimum of interference from other oxidizable species in solution. The interference of cupric ion could effectively be eliminated by the addition of hydrazine sulphate, but in about 50% of the cases, excessively low results were obtained indicating that some of the zinc ion had been effectively removed from solution. In most cases some cuprous sulphate precipitated after the addition of hydrazine and when the amount of this precipitate was large a considerable amount of zinc was carried down with it. For this reason, the use of hydrazine sulphate to eliminate the interference of copper can only be recommended in those cases where the amount of copper is much smaller than the amount of zinc present. In the analysis of most samples, however, it would be convenient to remove and/or determine the copper by electrolysis and then determine the zinc by titration with ferrocyanide, eliminating the remaining interferences with EDTA.

Zusammenfassung—Die Anwendung von ÄDTA in der Rolle des maskierende Mittels während der Titration von Zink mit Kaliumeisencyanür wurde untersucht. In Anwesenheit von ÄDTA und pH von 2,0–2,1 ist eine genaue Bestimmung von Zink neben Fe, Ni, Pb, und Al, möglich. Man kann aber die störung von Cu, Co, Cd, Mn, nicht eliminieren.

Résumé—Les auteurs ont étudié l'utilisation de l'EDTA comme agent de dissimulation dans le dosage du zinc par le ferro-cyanure de potassium. Si le pH est fixé à une valeur de 2 ou 2,1 et si on ajoute de l'EDTA, on peut doser le zinc avec précision en présence de fer, nickel, plomb et aluminium. Cependant cette méthode ne pourrait pas éliminer l'interférence du cuivre, du cobalt, du cadmium et du manganèse.

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NEW COLOUR TESTS FOR THE LARGER POLYNUCLEAR AROMATIC HYDROCARBONS

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Summary—An investigation of the reaction of the aromatic aldehyde-phosphorus pentachloride reagents with polynuclear aromatic hydrocarbons has shown that a number of aldehydes can be substituted for piperonal in this spectral test but only two were specific for the more basic aromatic compounds. The 9-anthraldehyde reagent gives intense bands in the 800–960 mμ spectral region with the larger hydrocarbons. The 3-nitro-4-dimethylaminobenzaldehyde reagent reacts readily in most cases with the benzene extract of air particulates. This procedure is ideal for the analysis of peri-condensed aromatic hydrocarbons.

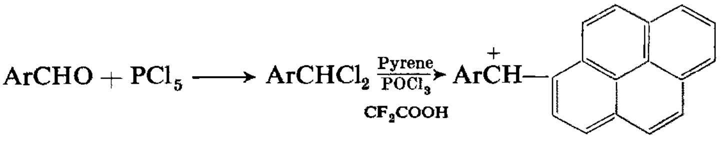
It was found that trifluoroacetic anhydride could be substituted for phosphorus pentachloride in the test reagent, but no particular advantage was incurred by this substitution.

INTRODUCTION

UNTIL recently simple colorimetric methods for the analysis of polynuclear aromatic hydrocarbons have been practically non-existent in the literature. With the piperonal chloride test, intensely brilliant, stable colours can be formed with aromatic and hetero-aromatic compounds which are more basic than benzene under the conditions of the test, and which have their highest electron density at an aromatic carbon atom.[1,2] Of great interest are the reactions of this reagent with the strongly carcinogenic 2-acetylaminofluorene,[3] 2-trifluoroacetylaminofluorene,[3] and benzo(a)pyrene[1] to give brilliant stable colours susceptible to quantitative study. The reagent has also been applied to the study of aromatic compounds in air particulate matter.[2]

Although piperonal chloride is an excellent general reagent for aromatic compounds, sensitive reagents are needed which are specific for a smaller group of compounds or for individual hydrocarbons of air pollution interest. With the desire to obtain a reagent specific for the larger polynuclear hydrocarbons, among which are found the vast majority of potent hydrocarbon carcinogens,[4] many aldehydes have been investigated.

In these colour tests the following reactions take place, e.g. with pyrene:



The phosphorus oxychloride serves as a catalyst. Without the added extra amount the sensitivities are not as good. The trifluoroacetic acid is necessary as a strongly acidic solvent, as a proton donor, and as a reaction initiator. The evidence indicates the formation of a diarylmethane dye.[1]

EXPERIMENTAL

Reagents and equipment

Trifluoroacetic acid was obtained from the Minnesota Mining and Manufacturing Co. Furfural was obtained from the Fisher Scientific Co. Indole-3-aldehyde, 2-thenaldehyde, 2-naphthaldehyde, 9-anthraldehyde, benzo(a)pyrene and benzo(g, h, i)perylene were obtained from the Aldrich Chemical Co. Perylene was obtained from the K and K Laboratories; benzo(e)pyrene from Terra Chemicals Inc., 500 Fifth Ave, New York 36, N.Y.; acenaphthene, pyrene, anthracene, chrysene, fluoranthene and trifluoroacetic anhydride from Matheson, Coleman and Bell, Norwood, Ohio. Anthanthrene, m.p. 258°, was prepared by the reduction[5] of anthanthrone (Aldrich Chemical Co.).

3-Nitro-4-dimethylamino-benzaldehyde was prepared by the following procedure. To a stirred solution of 15 g of *p*-dimethylaminobenzaldehyde in 150 ml of concentrated sulphuric acid was added 6.6 ml of nitric acid (d. 1.42) dropwise at 0–5°. The mixture was then poured into ice water. Crystallization from methanol gave an 80–90% yield of yellow needles, m.p. 103–105°, Lit. m.p.[6] 103–105°.

A Cary recording quartz spectrophotometer Model 11, and a Beckman Model DU spectrophotometer were used for wave length maxima determinations.

Aldehyde–PCl_5 *reagents*

Furfural: Fifty milligrams of furfural and 100 mg of phosphorus pentachloride were dissolved in 100 ml of chloroform with cooling.

2-*Thenaldehyde*: Fifty milligrams of this aldehyde and 100 mg of phosphorus pentachloride were boiled for 1 min in 20 ml of chloroform and then cooled. The solution was then diluted to 25 ml.

3-*Nitro*-4-*dimethylaminobenzaldehyde*: Fifty milligrams of the aldehyde and 500 mg of phosphorus pentachloride in approximately 20 ml of *o*-dichlorobenzene were heated at the boiling point until a clear solution was obtained. The solution was then cooled and diluted to 25 ml with *o*-dichlorobenzene.

9-*Anthraldehyde*: In a similar fashion 125 mg of the aldehyde and 250 mg of phosphorus pentachloride were boiled in approximately 20 ml of chloroform. The solution was cooled and diluted to 25 ml with chloroform.

Indole-3-*aldehyde*: Two hundred and fifty milligrams of the indole aldehyde was dissolved in 12 ml of *o*-dichlorobenzene by boiling the solution for 1 min; similarly 375 mg of phosphorus pentachloride was dissolved in 3 ml of *o*-dichlorobenzene. The cooled phosphorus pentachloride solution was added to the cooled solution of the aldehyde with stirring. The mixture was boiled for 1 min and then diluted to 25 ml with *o*-dichlorobenzene.

Procedure

(*a*) To 1 ml of the chloroform test solution was added 1 ml of the aldehyde-phosphorus pentachloride solution, 0.5 ml of phosphorus oxychloride, and trifluoroacetic acid to a final volume of 10 ml. After each addition the mixture was shaken gently to ensure complete mixing. The absorption spectrum was then determined against a blank of the same solvent-reagent composition. Only the more intense long wave length bands have been reported.

(*b*) *Trifluoroacetic anhydride method*: To 1 ml of a 2% solution of 2-naphthaldehyde in chloroform was added 0.1 ml of trifluoroacetic anhydride followed by 1 ml of the chloroform test solution. After the mixture was allowed to stand for 5 min, 1 ml of phosphorus oxychloride was added and the solution was diluted to 10 ml with trifluoroacetic acid. The absorption spectrum was then determined against a blank.

DISCUSSION OF RESULTS

Investigation of a large number of aldehydes has shown that in the test for aromatic compounds,[2] piperonal can be replaced by the following analogous aldehydes—anisaldehyde, veratraldehyde, *o*-methoxybenzaldehyde and 3:4:5-trimethoxybenzaldehyde with not too great a change in the sensitivity or wave length maxima.

TABLE I. 2-FURFURAL TEST FOR PERI CONDENSED AROMATIC HYDROCARBONS

Compound	$\lambda_{\max}$, *mμ*	Sensitivity[a]
Pyrene	535	0.04
	630	0.007
	670	0.005
Benzo(e)pyrene	573	0.007
	668	0.009
Benzo(a)pyrene	685	0.008
	743	0.007
Benzo(g, h, i)perylene	820	0.005
Anthanthrene	750s[b]	0.006
	787	0.005
Perylene	820	0.005

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.

[b] s = shoulder.

In a previous publication[7] it was predicted that aromatic aldehydetrifluoroacetic anhydride condensation products would be capable of detecting aromatic compounds in appropriate acidic media. The prediction was verified, for the 2-naphthaldehyde-trifluoroacetic anhydride procedure gave a wave length maximum of 805–810 mμ with a sensitivity of 0.007 for perylene and a wave length maximum of 685 mμ with

TABLE II. 2-THENALDEHYDE STET

Compound	$\lambda_{\max}$, *mμ*	Sensitivity[a]
Fluoranthene	585	0.020
Acenaphthene	623	0.008
Pyrene	630s[b]	0.006
	670	0.004
Benzo(e)pyrene	578	0.008
	684	0.008
Benzo(a)pyrene	705	0.006
	750	0.005
Benzo(g, h, i)perylene	760	0.007
Anthanthrene	560	0.014
	775	0.005
Perylene	825	0.005

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.

[b] s = shoulder.

approximately the same sensitivity for pyrene. Other aldehydes can be substituted in the test procedure, but this method does not appear to offer any particular advantage over the phosphorus pentachloride methods.

The simplest aldehydes found to react with polynuclear hydrocarbons under the conditions of the test are 2-furfural and 2-thenaldehyde. These reagents are not as powerful as piperonal in that they do not react with 2-acetylaminofluorene and analogous derivatives, while piperonal does.[3] On the other hand they do react with the peri condensed hydrocarbons and with some of the less basic ring systems such as fluoranthene and chrysene (Tables 1 and II). However, they do not have the necessary specificity under the conditions of the test.

TABLE III. INDOLE-3-ALDEHYDE TEST

Compound	λ_{max}, $m\mu$	Sensitivity[a]
1-Methoxynaphthalene	570	0.011
1-Naphthol	575	0.09
9-Ethylcarbazole	575	0.012
1-Anilinonaphthalene	597	0.007
Phenyl selenide	616	0.016
1-Anthrol	650	0.025
Anthrone	651	0.009
Benzo(e)pyrene	685	0.038
Pyrene	690	0.006
Benzo(a)pyrene	750	0.006
Anthanthrene	790	0.020
Perylene	830	0.006

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.

The indole-3-aldehyde reagent reacted readily with various types of aromatic compounds (Table III). This compound did not have the reactivity of piperonal or the required specificity. For indole-3-aldehyde as for all the other aldehydes, it is

TABLE IV. 9-ANTHRALDEHYDE TEST

Compound	λ_{max}, $m\mu$	Sensitivity[a]
Acenaphthene	790	0.010
Pyrene	850	0.008
Benzo(a)pyrene	860	0.012
Anthracene	860	0.010
Benzo(a)pyrene	910	0.008
Benzo(g, h, i)perylene	910	0.004
Anthanthrene	955	0.006
Perylene	965	0.010

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.

possible that by a proper manipulation of conditions much greater sensitivities could be obtained.

With the 9-anthraldehyde reagent the peri condensed aromatic hydrocarbons gave dyes absorbing at extremely long wave length, (Table IV). In this area the wave length maxima and the sensitivities are considered to be approximations. Note should be taken of the extremely long wave lengths at which anthanthrene and perylene are analyzed. Benzene, toluene, xylene, biphenyl, fluorene, chrysene and fluoranthene were found to be essentially insensitive to this reagent. These results suggest that aromatic compounds weaker than, or of the same order of basicity as chrysene do not react with the reagent.

TABLE V. 3-NITRO-4-DIMETHYLAMINOBENZALDEHYDE TEST

Compound	$\lambda_{\max}$, $m\mu$	Sensitivity[a]
Acenaphthene	618	0.010
Pyrene	702	0.003
Benzo(e)pyrene	710	0.020
3-Methylcholanthrene	743	0.016
Anthracene	748	0.013
Benzo(a)pyrene	770	0.005
Benzo(g, h, i)perylene	770	0.030
Anthanthrene	845	0.005
Perylene	860	0.006

[a] Micromoles in 3 ml of solution giving an absorbance of 0.1 in a 1-cm cell.

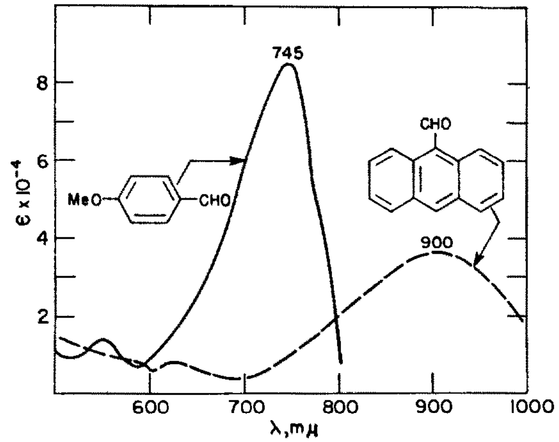


FIG. 1. Aromatic aldehyde-phosphorus pentachloride tests for benzo(a)pyrene. Anisaldehyde (——); Anthraldehyde(- - -).

Of all the aldehydes so far tested 3-nitro-4-dimethylaminobenzaldehyde appears to be the best for the polynuclear aromatic hydrocarbons, (Table V). It must be emphasized that the anthraldehyde and 3-nitro-4-dimethylaminobenzaldehyde tests are not in the strict sense colour tests, for the colours obtained in the analysis of the larger polynuclear aromatic hydrocarbons are not due to the main band but to weak secondary visible bands. The main band is out of the visible region of the spectrum, so the resultant "colour" due to this absorption band cannot be seen by the human eye. The 3-nitro-4-dimethylaminobenzaldehyde test was the most thoroughly investigated. It was found to give negative results with the following compounds: benzene, toluene, *m*-xylene, mesitylene, durene, biphenyl; *p*-terphenyl, fluorene, naphthalene, phenanthrene, fluoranthene, triphenylene, chrysene, picene, stilbene, phenol and anthrone. The vast majority of these compounds react with piperonal chloride. Like 9-anthraldehyde this reagent reacts with the more basic larger polynuclear aromatic hydrocarbons. With all of these aldehyde reagents, except 9-anthraldehyde, the carcinogenic benzo(a)pyrene reacts to give an intense band near 750 mμ. With 9-anthraldehyde a fairly intense band at about 910 mμ is obtained. This latter test for benzo(a)pyrene is compared with the anisaldehyde method in Fig. 1.

When the benzene-soluble extract of a Cincinnati air particulates sample was reacted in the 3-nitro-4-dimethylaminobenzaldehyde test, a strong band was obtained near 790 mμ. This indicates the predominance of the larger polynuclear aromatic hydrocarbons with ring systems containing 3 to 5 fused rings. Separation of the neutral aromatic fraction from this benzene soluble extract by standard procedure[8] and reaction of this fraction in the test gave a strong band at 850 mμ. This indicates that of the large polynuclear aromatic hydrocarbons in the aromatic fraction the 5-, 6- and probably 7-membered fused ring structures predominate.

Zusammenfassung—Eine Untersuchung der Reaktion der aromatischen Aldehydphosphorpentachlorid-Reagens mit polykernaromatischen Kohlwasserstoffen hat gezeigt, dass manche Aldehyde den Piperonal in dieser Spektral-photometrischen Methode substitutieren können, aber nur zwei Aldehyde für die mehr-basischen aromatischen Verbindungen spezifisch sind. Das 9-Anthraldehyd-Reagens zeigt intensive Bänder bei 800–960 mμ mit Kohlenwasserstoffen von höheren C-Zahl. Das 3-Nitro-4-dimethylaminobenzaldehyd-Reagens reagiert glatt mit Benzol-Extraktion von Luft-Partikelchen. Dieses Verfahren ist wahrscheinlich die erste analytische in dem Infraroten-Bereich angewandte Methode. Man kann Trifluoro-essig-anhydrid für Phosphor-pentachlorid in Reagensmischung substitutieren. Es wurden jedoch dabei keine besondere Vorteile beobachtet.

Résumé—Une étude de réaction entre les réactifs du type aldéhyde aromatique-penta chlorure de phosphore et les hydrocarbures aromatiques polynucléaires, a montré qu'un certain nombre d'aldéhydes peuvent remplacer le piperonal dans ce test spectrophotométrique, mais seuls deux d'entre eux sont spécifiques pour les composés aromatiques les plus basiques. Le réactif au 9-anthraldehyde donne des bandes intenses dans la région spectrale 800–960 mμ avec les hydrocarbures supérieurs. Le réactif au nitro-3-diméthyl-4-aminobenzaldehyde réagit presque toujours facilement avec les composés que donnent les particules de poussière dans l'air par extraction avec le benzène.

Ce procédé est probablement la première méthode analytique utilisant des longueurs d'onde en dehors de la région visible du spectre dans le proche infra-rouge. On a trouvé que l'anhydride trifluoroacétique pouvait remplacer le penta chlorure de phosphore dans le réactif-test, mais il n'y a aucun avantage particulier à cette substitution.

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AN ELECTROCHEMICAL SEPARATION PROCESS FOR USE IN POLAROGRAPHY*

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Summary—A simple electrochemical method is described whereby metals which are soluble in mercury can be analysed polarographically for traces of more electronegative impurities. The technique was specifically developed for the analysis of bismuth using a square wave polarograph and full details, both experimental and theoretical, are given in this case. Other possible uses of the method in the analysis of mercury-soluble metals employing both conventional and square wave polarographs and also in the analysis of aqueous salt solutions are suggested.

INTRODUCTION

It is well known that considerable difficulty is encountered in direct current polarography when attempting to estimate the concentration of a minor constituent of a mixture in the presence of a more readily reducible major constituent. This problem is frequently encountered in metallurgical analysis, where, for example, one might wish to estimate the amount of zinc present in a sample of cadmium[1,2,3] or lead[4]. Usually the major constituent must be removed from the mixture before the polarographic analysis can be carried out.

Because of the derivative form of polarograms obtained with alternating current polarographs a considerable improvement in mixture analysis is achieved. Loss of sensitivity, however, will result if the ratio of the concentration of the more readily reducible major constituent to that of the minor constituent becomes too large. This loss of performance may be caused by irregular motion of the surface of the mercury drop, by the wave arising from the electropositive substance becoming so large that it overlaps other waves and by the failure of the electronic circuits of the polarograph to handle the large direct current flowing. It may therefore still be desirable and even necessary to carry out some preliminary separation procedure in low level determinations of trace impurities in metals.

In this paper a simple separation procedure is described which is of particular value in the polarographic analysis of metals such as bismuth, lead and cadmium, that dissolve readily in mercury. The method was specifically developed for the analysis of bismuth using a square wave polarograph[5] and the experimental procedure used in this case is described later in some detail. Other possible applications in both a.c. and d.c. polarography are also outlined.

ANALYSIS OF BISMUTH WITH A SQUARE WAVE POLAROGRAPH

Introduction

The square wave polarograph can be used to estimate the concentration of a minor constituent in the presence of a 10^5-fold excess of a more readily reducible

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* This paper was presented at a meeting of the Polarographic Society, held at Nobel Division, Imperial Chemical Industries Ltd., Stevenston, Ayrshire, on 26 September, 1958.

major constituent provided that the concentration of the latter constituent does not exceed $\sim 10^{-2}M$. This means, therefore, that in the analysis of bismuth by dissolution of the metal in acid and subsequent dilution to $10^{-2}M$ with respect to bismuth, it is possible to estimate electronegative impurities whose concentration in the final solution is $10^{-7}M$. Thus the concentration of these impurities in the original metal must not be less than $\sim$10 ppm if they are to be estimated with any degree of accuracy. In any case $10^{-7}M$ is close to the lower level of concentration of even a single substance to which the square wave polarograph can be applied qualitatively. Also, impurities which might be as high as $10^{-6}M$ may be introduced by the reagents and supporting electrolyte. Thus to determine the concentration of low level ($<$10 ppm) impurities in bismuth with the square wave polarograph, some preliminary separation process must be employed.

Methods which have been used in the past have involved the dissolution of the bismuth metal sample into a suitable medium, followed by the removal of almost all bismuth by precipitation, volatilisation or electro-deposition at controlled potential.[6] The first and second of these methods are subject to the possibility of losses during the separation stages. Also, the addition of the various reagents may complicate the polarographic analysis of the final solution. Although the electrodeposition method does not have either of these disadvantages it is rather tedious to perform experimentally.

It was with these points in mind that the following simple technique was developed. It is based on electrochemical principles and is much easier to carry out than the electrodeposition method mentioned above.

If pure bismuth is dissolved in mercury and the resulting amalgam contacted with, for example, *M* hydrochloric acid solution containing some Bi^{3+} ions, the amalgam takes up a potential controlled by the relative concentrations of bismuth metal and bismuth ions in the amalgam and solution phases respectively. This potential will not be greatly affected when the bismuth contains trace impurities. If the standard potential of the electrode reaction $M(Hg) = M^{n+} + nE$ where M is some metallic impurity (originally in the bismuth but now dissolved in the amalgam), is more negative than the actual amalgam potential, the metal M will tend to pass from the amalgam to the aqueous phase. In this way separation of the electronegative impurities from the bismuth will be obtained and the aqueous phase can be examined polarographically. The concentration of bismuth in the aqueous phase can be controlled by the previous addition to the solution of a calculated quantity of mercurous chloride. The mercurous ion is reduced by the amalgam forming mercury metal which dissolves in the amalgam and an equivalent amount of bismuth is oxidised and passes into the solution.

EXPERIMENTAL

10 ml of mercury were placed in a stoppered glass tube (1 cm diameter, 12·5 ml volume) and covered with 2 ml of *M* hydrochloric acid containing 0·4% mercurous chloride. One gram of bismuth, in small pieces was dropped through the acid layer into the mercury. Nitrogen was passed over the solution surface for some time and the tube was then quickly stoppered.* The tube was then gently shaken until the bismuth had completely dissolved in the mercury, the mercury being heated if necessary. The tube was then vigorously shaken for a further 15 minutes, and finally a known volume

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* Oxygen must be removed from the gas space above the aqueous phase to avoid oxidation of the bismuth amalgam and the concomitant formation of hydrogen peroxide.

of the acid layer was rapidly removed with a dry pipette and placed in a small polarographic cell. After deoxygenation square wave polarograms were recorded in the usual way, making standard additions to determine the concentrations of the various impurities.

Some typical square wave polarograms for the determination of lead in bismuth are shown in Figures 1 and 2. Figures 1(a) and (b) were both obtained at $\frac{1}{32}$ maximum sensitivity and refer respectively to bismuth samples taken before and after purification. The wave height of Figure 1(a) corresponds to ~3 ppm of lead in the original bismuth sample. Figure 2 is a polarogram from the same solution as in Figure 1(b) but at an increased sensitivity of $\frac{1}{4}$ maximum. The indicated concentration is here ~0·5 ppm and the height of this wave can be estimated with an accuracy of better than ±2%.

Discussion

For the experimental conditions outlined above the concentration of bismuth in the amalgam phase is $\sim 0{\cdot}5M$ and in the aqueous phase $\sim 5 \times 10^{-3}M$. If the bismuth originally contains a metallic impurity at a level of 10 ppm and all this impurity is transferred to the aqueous phase, its concentration in the latter phase will be $\sim 2{\cdot}5 \times 10^{-5}M$. Compared therefore, with the case where the bismuth is dissolved directly and then diluted to $10^{-2}M$, the concentration of the impurity in the final solution has increased 250 times, whereas the bismuth concentration has gone down by a factor of 2. It would, on paper at least, appear to be possible to determine impurities down to 0·1 ppm with an accuracy of ±2% in a bismuth sample using this amalgamation technique in conjunction with a square wave polarograph. In very low level determinations it will, of course, be necessary to carry out a blank experiment in the absence of bismuth.

To discover which metallic impurities can be determined in bismuth by this method some information regarding the potential of the bismuth-mercury amalgam must be obtained. From the Nernst equation it follows that

$$E^A = E_0^A - \frac{RT}{3F}\ln\frac{C_A^{\mathrm{Bi}}}{C_S^{\mathrm{Bi}}}\text{ volt} \qquad (1)$$

where E^A = amalgam potential,

$C_S^{\mathrm{Bi}} C_A^{\mathrm{Bi}}$ = concentration of bismuth in the solution and amalgam phases respectively,

and E_0^A = standard potential of the reaction $\mathrm{Bi(Hg)} = \mathrm{Bi}^{3+} + 3E$.

Thus, since $C_A^{\mathrm{Bi}} \doteq 0{\cdot}5M$ and $C_S^{\mathrm{Bi}} \doteq 5 \times 10^{-3}M$

$$E^A \doteq E_0^A \doteq 0{\cdot}039\text{ volt} \qquad (2)$$

For $\geqslant 99{\cdot}5\%$ transfer at equilibrium of a metallic impurity M from the amalgam to the aqueous phase, when the volume of the amalgam is five times that of the solution the Nernst equation predicts that

$$E^A \geqslant E_0^M + \frac{3RT}{nF}\text{ volt} \qquad (3)$$

where E_0^M = Standard potential of the electrode reaction $\mathrm{M(Hg)} = \mathrm{M}^{n+} + nE$. In the case where $n = 2$

$$E^A \geqslant E_0^M + 0{\cdot}088\text{ volt} \qquad (4)$$

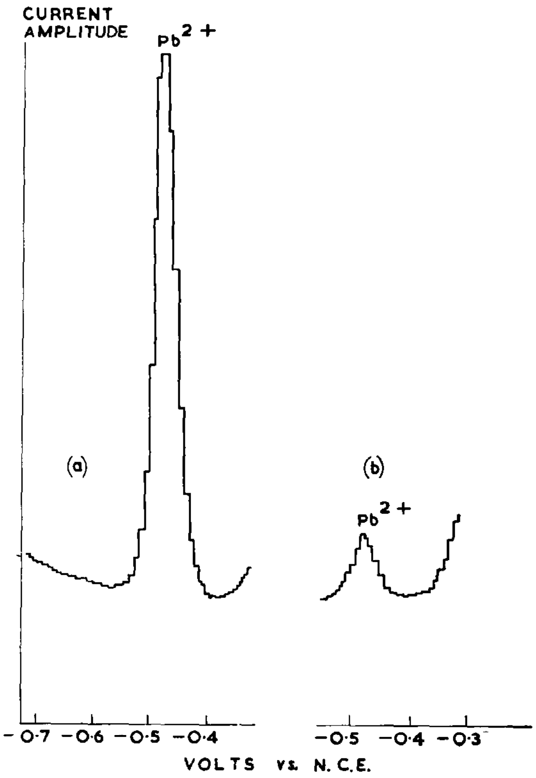

FIG. 1

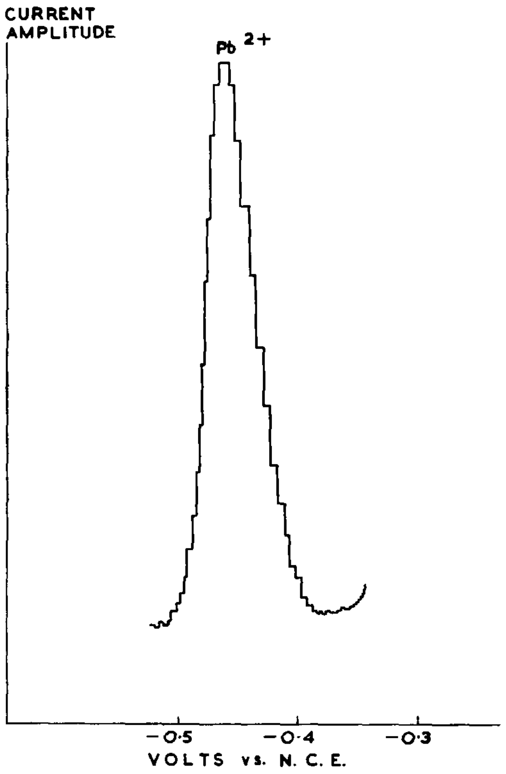

FIG. 2

FIGS. 1, 2. Square wave polarograms obtained in the analysis of bismuth for lead.

and therefore from equations (3) and (4)

$$E_0^M \leqslant E_0^A - 0{\cdot}127 \text{ volt} \tag{5}$$

It may be assumed for simplicity that for reversible electrode processes E_0^M and E_0^A are equal to the corresponding polarographic half wave potentials. Thus for 99·5% transfer of metal M to the aqueous phase the half-wave potential for M^{2+} in the medium in question (in this case *M* hydrochloric acid) must be at least 0·13 volt more negative than the half-wave potential for the reduction of bismuth ions from the same medium. For impurities which form univalent ions (*i.e.* $n = 1$) the calculated potential difference for 99·5% extraction is slightly greater than 0·2 volt. This means that cadmium, indium, lead, thallium and zinc can all be estimated by the amalgamation method. Copper, however, which is somewhat more electropositive than bismuth, cannot be determined.

Different metals will be extracted from the amalgam simultaneously if the relevant electrode reactions are polarographically reversible as the rate of extraction of each metal is then diffusion controlled.

OTHER APPLICATIONS

The analysis of cadmium for zinc has been carried out using the amalgamation technique and a square wave polarograph. The experimental procedure as outlined above was modified slightly as follows. One g of cadmium metal was dissolved in 10 ml of mercury and extracted with 5 ml of slightly acidified (pH = 2) *M* potassium chloride containing 0·25% calomel. A polarogram obtained in this way is shown in Figure 3(a), the sensitivity being ¼ maximum. The zinc wave indicates 0·5 ppm of zinc in the original cadmium metal. For comparison Figure 3(b) shows the polarogram obtained (¼ maximum sensitivity) for a solution ($10^{-2}M$ Cd^{2+}) prepared by dissolving a sample of the same cadmium metal in hydrochloric and nitric acids, evaporating to dryness several times with hydrochloric acid, and dissolving the residue in *M* KCl (pH 2). A blank experiment indicated that the small zinc wave in Figure 3(b) arose from impurities in the reagents used.

So far only the application of this separation technique to square-wave polarography has been investigated but there is little doubt that it could be used with advantage in conventional direct current polarography. As an example the analysis of bismuth containing 0·2% lead may be considered. By following the experimental procedure outlined above for bismuth a solution containing $5 \times 10^{-3}M$ bismuth and $5 \times 10^{-3}M$ lead would be obtained. If this solution were diluted 5 times with water and polarographed, the lead concentration could be accurately determined.

Other examples of metal analysis which could be treated similarly are the determination of cadmium and zinc in lead and of zinc in thallium. The method is, of course, not suitable for the analysis of metals which are insoluble or only slightly soluble in mercury, such as copper, iron and silver.

The technique can also be extended to the determinations of trace impurities in salt solutions. Suppose that 20 ml of a deoxygenated salt solution (for example, saturated sodium carbonate) are shaken vigorously with 10 ml of mercury containing $10^{-3}M$ zinc of "specpure" quality. This dilute zinc amalgam takes up a potential close to the zinc half-wave potential and all the more electropositive impurities (Cu, Pb, Cd, etc.) in the solution are reduced and pass into the amalgam phase. The amalgam is then separated from the solution and shaken with 2 ml of *M* hydrochloric acid containing somewhat more mercurous chloride than is required to oxidise all the zinc. The impurities in the amalgam are transferred, along with the zinc, to the acid which can be analysed polarographically. The zinc wave does not interfere with the waves obtained from the more electropositive elements. In this way the impurity concentrations are increased by a factor of 10 and they are also transferred to a more satisfactory supporting electrolyte.

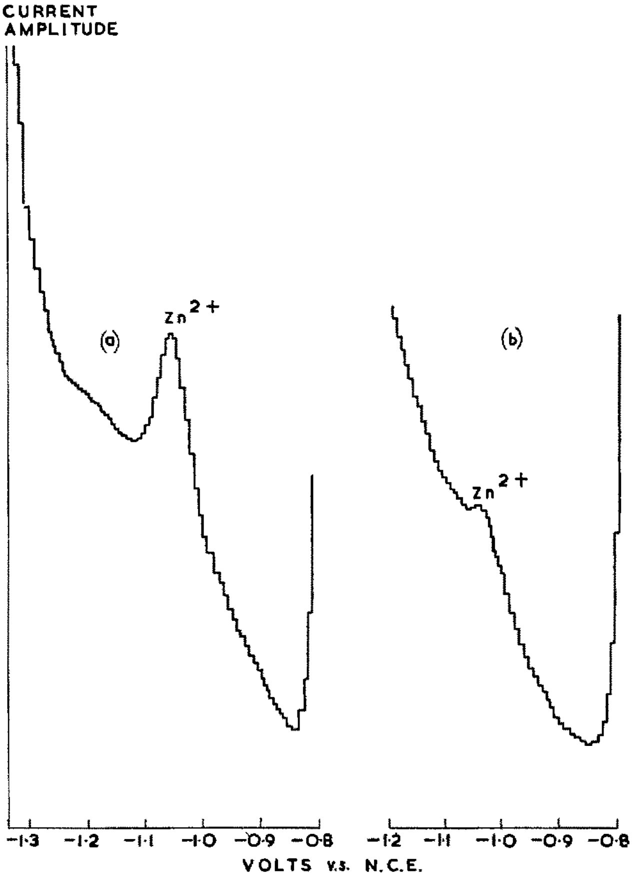

FIG. 3. Square wave polarograms obtained in the analysis of cadmium for zinc.

CONCLUSION

Although as yet little use has been made of these simple techniques, they can clearly be used with any type of polarograph to obtain improved sensitivity and greater freedom from troubles associated with impurities in the reagents used in the preparation of solutions.

Zusammenfassung—Eine einfache elektrochemische Methode wurde beschrieben womit die in Quecksilber lösliche Metalle für Spuren-Verunreinigungen polarographisch analysiert werden können. Die Methode wurde zur Analyse von Wismuth mittels des "Square-Wave" Polarographs entwickelt, und die experimentelle und theoretische Grundlagen wurden erörtert. Die andere Anwendungen der Methode wurden beschrieben.

Résumé—Une méthode électrochimique simple est décrite permettant l'analyse polarographique de métaux solubles dans le mercure en présence de traces d'impuretés plus électronégatives. La technique a été développée spécifiquement pour le bismuth en utilisant un polarographe à tension carrée et de nombreux détails ont été donnés dans ce cas, aussi bien au point de vue expérimental qu'au point de vue théorique. Il est suggéré d'autres utilisations possibles de la méthode pour l'analyse de métaux solubles dans le mercure et de solutions salines aqueuses en employant soit le polarographe classique soit le polarographe à tension carrée.

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THE PRECIPITATION OF NICKEL^{II} SULPHIDE FROM ACID SOLUTIONS BY THIOACETAMIDE

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Summary—Rate measurements have shown that the precipitation of nickel^{II} as sulphide by thioacetamide from solutions having hydrogen ion concentrations ranging from 0.3 to 1×10^{-7} molal conforms to the expression

$$-\frac{d\,[\mathrm{Ni^{II}}]}{dt} = k\,[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]/[\mathrm{H^+}],^{\frac{1}{2}}$$

where k is equal to 2.2×10^{-4} litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ min^{-1} at 90°. No hydrolysis controlled precipitation was observed. The energy of activation for the reaction, in the range 70°–90°, was calculated to be 20.8 kcal per mole. Precipitation conforming to this rate expression occurred at hydrogen ion concentrations at which precipitation by hydrogen sulphide was not obtained.

The effectiveness of the separation of lead^{II} and cadmium^{II} from nickel^{II} by the use of thioacetamide in solutions of pH 1 and 2 and maintained at 90° was studied. The rate of formation of nickel sulphide conformed to the above rate expression and was independent of the quantity of metal sulphide present, and of the concentrations of lead^{II}, cadmium^{II}, and of hydrogen sulphide in the reaction solution. The amount of nickel sulphide precipitated with cadmium and lead sulphide by means of the direct reaction between nickel ion and thioacetamide exceeded that co-precipitated when cadmium and lead were precipitated by hydrogen sulphide. However, under properly controlled conditions effective separations can be made.

INTRODUCTION

THE work reported in this paper is part of the general investigation being made in these laboratories of the use of thioacetamide as a precipitant for metal sulphides and as a means for effecting the precipitation of sulphides from homogeneous solutions. This type of precipitation may make it possible to improve certain existing sulphide separations and, especially in the case of nickel, to obtain sulphide precipitates which are more easily handled than those normally encountered.

Previous investigations of the reactions of thioacetamide and its products of hydrolysis with lead^{II},[9] arsenic^{III} and arsenic^{V},[3] and cadmium^{II},[2] have been made. The rate of precipitation of both cadmium^{II} and lead^{II} at hydrogen ion concentrations greater than 10^{-3} M is controlled by the rate of hydrolysis of the thio group of the thioacetamide to give hydrogen sulphide and this rate is first order with respect to the thioacetamide and to the hydrogen ion concentrations. Precipitation by this means is designated as "hydrolysis controlled." The hydrolysis reaction has been assumed to consist of the attack of hydrogen ion upon the thioacetamide molecule and subsequent formation of hydrogen sulphide as the rate determining step. The reaction of the cation with the hydrogen sulphide to form a sulphide precipitate is apparently relatively rapid under the conditions studied.

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* Contribution No. 2427 from the Gates and Crellin Laboratories of Chemistry. Communications concerning this article should be addressed to E. H. Swift.

At lower hydrogen ion concentrations a precipitation reaction which is first order with respect to both the cation and the thioacetamide concentrations and inversely half-order with respect to the hydrogen ion concentration becomes predominant and rate controlling. The mechanism of this reaction is not yet understood. It is called the "direct reaction" to distinguish it from the "hydrolysis controlled" reaction.

No evidence for this direct reaction was found in studies of the precipitation of arsenic^{III}; the rate of precipitation of the sulphide appeared to be hydrolysis controlled even at pH 6. Arsenic^{V} is reduced to arsenic^{III} before precipitation of the sulphide by thioacetamide.

Although analytical studies[1,4] of the precipitation of nickel from ammoniacal solutions by thioacetamide have been made, there seems to have been no previous work on the precipitation of nickel by thioacetamide from acid solutions. This paper presents the results of a study of the precipitation of nickel sulphide by thioacetamide from acid solutions under various conditions and of the separation of cadmium and lead from nickel by the use of this reagent.

EXPERIMENTAL

Reagents

Reagent grade chemicals were used.

Thioacetamide solutions, 1.00 *VF* (volume formal, formula weights per litre), were prepared from Arapahoe Lot No. 1402 material. Although these solutions remained clear and colourless for longer times, they were freshly prepared at two-week intervals.

Solutions of *cadmium nitrate, lead nitrate* and *nickel^{II} nitrate,* each 0.100 *VF,* were prepared by weight.

Perchloric acid and carbonate-free *sodium hydroxide* solutions were prepared and standardized by conventional methods.

A neutral 0.1 *VF* solution of *dimethylglyoxime* in ethanol was used.

The *hydrogen phthalate-phthalate buffer solutions* were prepared by adding calculated weights of potassium hydrogen phthalate to constant volumes of sodium hydroxide solution. These buffer solutions were diluted to a given volume in order to form the stock buffer solutions.

Sodium nitrate, 0.10 *VF,* was used to provide constancy of ionic strength, although later experiments revealed no significant ionic strength effect.

Apparatus

The apparatus used for the quantitative study of the rate of precipitation of nickel sulphide was similar to that described by Swift and Butler.[9] Most of the rate measurements were made at 90 ± 1°.

The separations of cadmium and lead from nickel were carried out in 15 × 125-mm test tubes and 25-ml Erlenmeyer flasks placed in a water bath maintained at 90 ± 1°.

Procedure

The more quantitative studies in the pH range 5–7 were made by mixing in a reaction tube measured volumes of the stock solutions of thioacetamide, nickel nitrate, and buffer. Enough sodium nitrate to attain an initial ionic strength of 0.40 was added and the solution diluted to 100 ml. The reaction tube was then placed in the constant temperature bath and 12-ml portions were removed at timed intervals. These portions were cooled in order to quench the reaction, centrifuged, and duplicate 5.00-ml samples of the clear centrifugate transferred to 15 × 125-mm test tubes.

An excess of 6 *VF* ammonium hydroxide was added to each sample, and the sample tubes were then placed in hot water in order to precipitate the nickel as sulphide. A coarse, easily separated precipitate was formed. The mixture was cooled and centrifuged. The centrifugate was drawn off and discarded.

The precipitate was first heated in a water bath with 1 ml of 9 *VF* perchloric acid and five drops of 6 *VF* nitric acid, then heated to fuming over a flame until all the precipitate had dissolved and any oxides of nitrogen were expelled. The solution was cooled and diluted to 2 ml with water. Five drops of 0.007 *VF* methyl red were added, and the solution adjusted to the transition colour by the alternate additions of 6 *VF* and 0.1 *VF* sodium hydroxide and 0.1 *VF* perchloric acid solutions. Comparison solutions were used in order to obtain this colour more exactly. An excess of 0.1 *VF* dimethylglyoxime solution was added, and the flocculent red precipitate centrifuged.

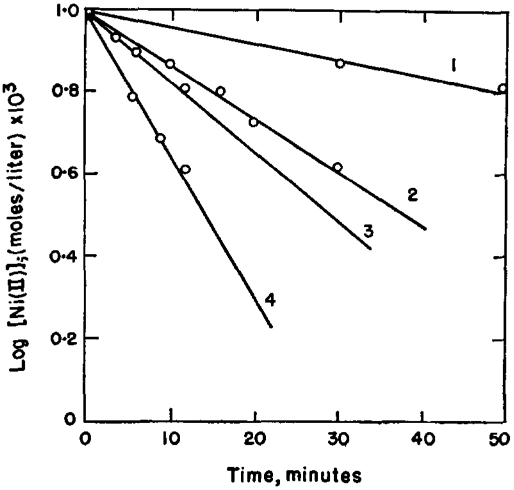

Fig. 1. Effect of nickel^{II} concentration on the rate of nickel sulphide precipitation. Initial thioacetamide: 0.10 *VF*; initial nickel^{II}: 0.010 *VF*; temperature: 90°.

1. pH 5.0   3. pH 6.5
2. pH 6.2   4. pH 7.1

If over two milligrams of nickel were judged to be present in the precipitate, a titration with 0.030 *VF* sodium hydroxide solution was made to the methyl red transition colour. The red precipitate interfered with the detection of this colour, particularly near the end-point, unless the mixture was centrifuged at intervals during the titration. This method of analysis was checked with known quantities of nickel^{II} similar to those which were present in the precipitates, and the average deviation in the results was less than 1 % provided comparison solutions were used.

When the quantity of nickel in the dimethylglyoxime precipitate was judged by visual inspection to be less than 2 mg, the estimation was made by comparing the volume of the centrifuged precipitate with known quantities of nickel precipitated under the same conditions. The accuracy of confirmatory estimations made with these quantities of nickel was within ±10% and was superior to the titrimetric method.

In the study of the rate of nickel precipitation and its separation from cadmium and lead at low pH values, 10 ml of reaction solution were prepared by mixing measured quantities of thioacetamide, metal nitrates and perchloric acid in each vessel. These vessels were then placed in a bath, at 90°, and removed at timed intervals. The reaction was quenched by cooling the reaction tube, and the precipitate separated by centrifuging the mixture. The clear centrifugate was discarded and the precipitates washed thoroughly by decantation. The precipitates were analyzed as described above. In those samples containing lead, however, the lead sulphate resulting from the dissolution step was removed by decanting the centrifugate before proceeding with the analysis.

RESULTS AND DISCUSSION

The precipitation from acid solutions

In preliminary qualitative experiments a very *slow* formation of nickel sulphide was observed at 90° in solutions 0.01 *VF* in nickel^{II}, and 0.10 *VF* in thioacetamide and in which the hydrogen ion concentration ranged from 0.3 *VM*–0.01 *VM*. In the same time interval similar solutions saturated with gaseous hydrogen sulphide, but containing no thioacetamide, gave *no* precipitate.

Rate measurements at pH *values 5–7*

Measurements of the rate of precipitation were made in the pH range 5.0–7.1 and at 90°. In this pH range and at this temperature the precipitation took place at conveniently measurable rates and the results obtained could be readily compared with those found in previous studies.[2,3,9] The effects of the concentrations of nickel$^{\text{II}}$, thioacetamide, and hydrogen ion upon the rate of precipitation were evaluated in order to formulate a rate expression and to calculate a rate constant. These measurements were made in the presence of phthalate buffer systems. The agreement with those of subsequent measurements in perchloric acid solutions, described later, indicated that the phthalate buffer did not exert any significant effect on the rate of the direct reaction.

Effect of the nickel$^{\text{II}}$ concentration

As is shown in Figure 1, plots of the logarithm of the nickel$^{\text{II}}$ concentration versus the reaction time at various hydrogen ion concentrations were linear; thus it appears that the precipitation reaction is first order with respect to the nickel$^{\text{II}}$ concentration at 90°.

TABLE I.—EFFECT OF THIOACETAMIDE ON THE RATE OF PRECIPITATION OF NICKEL SULPHIDE

Initial nickel$^{\text{II}}$: 0.010 *VF*, pH 6.4, $t = 90°$

(CH_3CSNH_2), *VM*	k_1[a]	$k_2 \times 10^4$[b] (*litre*$^{\frac{1}{2}}$ *mole*$^{-\frac{1}{2}}$ *min*$^{-1}$)
0.050	0.0177	2.25
0.100	0.0342	2.21
0.150	0.0553	2.31
0.200	0.0733	2.31
0.250[c]	0.0774	2.19
0.300	0.1068	2.26

Average $(2.25 \pm 0.05) \times 10^{-4}$

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = k_1[\mathrm{Ni^{II}}].$$

[b] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = k_2\frac{[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}}$$

[c] Measurements at pH 6.3.

Effect of the thioacetamide concentration

Table I presents a tabulation of the rate constants calculated from a series of experiments made to determine the effect of the thioacetamide concentration upon the rate of precipitation. The constancy of these values shows that in the range of concentrations studied, 0.050 *VF* to 0.30 *VF* in thioacetamide, the rate of the reaction is first order with respect to the thioacetamide concentration.

Effect of the hydrogen ion concentration

The effect of the hydrogen ion concentration on the rate of precipitation was studied over the range from 1 × 10^{-5} *VM* to 10^{-7} *VM*. Haring and Westfall[5] reported. that quantitative precipitation of nickel sulphide can be made in this range by means of hydrogen sulphide. Therefore, in some experiments, nitrogen was bubbled through the reaction solution in order to remove the hydrogen sulphide formed by the hydrolysis of the thioacetamide; in these experiments no significant change in the rate of precipitation was observed. The rate constants calculated from these measurements are given in Table II, and show that the reaction has an inverse half-order dependency upon the hydrogen ion concentration. In none of these experiments was there evidence of hydrolysis controlled precipitation. Some precipitation by the hydrogen sulphide resulting from the acid hydrolysis of thioacetamide is to be expected at pH values between approximately 5 and 2; however, rate measurements were not attempted in this pH range since the rate of this precipitation would not be likely to conform to the acid hydrolysis rate expression because of supersaturation effects.

Table II.—Effect of hydrogen ion on the rate of precipitation of nickel sulphide by thioacetamide

Initial nickel^{II}: 0.01 *VF*; initial thioacetamide: 0.10 *VF*, $t = 90°$

pH	k_1[a]	$k_2 \times 10^4$ [b]
7.1	0.078	2.21
6.5	0.039	2.23
6.4	0.034	2.21
6.2	0.029	2.30
5.0	0.006	2.14

Average (2.22 ± 0.05) × 10^{-4}

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni}^{\mathrm{II}}]}{dt} = k_1\,[\mathrm{Ni}^{\mathrm{II}}]$$

[b] Calculated from the expression

$$-\frac{d[\mathrm{Ni}^{\mathrm{II}}]}{dt} = k_2\,\frac{[\mathrm{Ni}^{\mathrm{II}}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H}^+]^{\frac{1}{2}}}$$

The rate expression

The data from the above measurements indicate that under the conditions of these experiments the precipitation of nickel sulphide by thioacetamide takes place by a direct reaction similar to those reported for lead[9] and cadmium.[2] The rate expression for this reaction is

$$-\frac{d[\mathrm{Ni}^{2+}]}{dt} = \frac{k\,[\mathrm{Ni}^{2+}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H}^+]^{\frac{1}{2}}} \qquad (1)$$

and the calculated rate constant, k, is 2.2 × 10^{-4} litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ min^{-1} at 90°.

The energy of activation

In order to calculate the energy of activation the rates of this direct reaction were measured at 70° and 80° and the constants were calculated to be 8.95 × 10^{-5} and

1.45×10^{-4} litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ min^{-1}, respectively. From these values and that calculated at 90°, the energy of activation was calculated to be 20.8 ± 0.8 kcal per mole. This value is approximately the same as that calculated for the precipitation of cadmium sulphide.[2]

The precipitation of nickel sulphide at pH *values of* 1 *and* 2

Precipitations by direct reactions were not observed at pH 1 and 2 with lead[9] and cadmium[2] because such reactions would have been masked by the predominant hydrolysis controlled reaction. However, since no evidence of the hydrolysis controlled precipitation was observed with nickel in preliminary experiments, a check for precipitation by the direct reaction could be made at these hydrogen ion concentrations.

It was found that no precipitates were formed when solutions 0.040 *VF* in nickel^{II} and having pH values of 1 and 2, established by means of perchloric acid, were saturated with hydrogen sulphide and maintained at 90° for one hour. In addition, solutions of the same composition were saturated with H_2S and maintained for 70 hrs at room temperature without visible evidence of a nickel sulphide precipitate. However, when solutions 0.040 *VF* in nickel^{II} and 0.40 *VF* in thioacetamide and having the same pH values were maintained at 90°, nickel sulphide was slowly formed. In other cases hydrogen sulphide was added to similar solutions but no change in the rate of precipitation of nickel sulphide was observed. The data given in Table III show that the amounts of nickel^{II} found in the precipitates agree with those calculated by Expression 1 within the limits of the accuracy of the measurements. Experiments in which cadmium or lead sulphide precipitates were present showed that these did not alter the rate of nickel sulphide precipitation. Therefore, it was concluded that nickel sulphide is precipitated by the direct reaction at these hydrogen ion concentrations,

TABLE III.—EXPERIMENTAL VS. CALCULATED WEIGHTS OF NICKEL PRECIPITATED AS SULPHIDE BY THE DIRECT REACTION AT pH 1 AND 2

Initial $Ni(NO_3)_2$: 0.04 *VF*, initial CH_3CSNH_2: 0.40 *VF*, $t = 90°$

Time, *min*	Nickel precipitated as NiS, *mg*	
	Found	Calculated[a]
pH 1		
5	0.04	0.04
12	0.15	0.09
pH 2		
12	0.16	0.24
24	0.46	0.48
28	0.58	0.56
60	1.35	1.2
120	2.15	2.1

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = 2.2 \times 10^{-4} \frac{[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}}$$

and that *it is possible to precipitate nickel sulphide by thioacetamide at higher hydrogen ion concentrations than precipitation can be obtained with hydrogen sulphide—at least in comparable times.*

Additional experiments were made with solutions initially 0.4 *VF* in nickel^{II}, 0.40 *VF* in thioacetamide, and 0.3 *VF* in perchloric acid to ascertain if the direct reaction would cause precipitation at this hydrogen ion concentration. Under these conditions the hydrolysis of the thioacetamide would cause its concentration to be decreased to 0.2 *VF* within ten minutes,[9] and the solution would be saturated with hydrogen sulphide. After twenty minutes the quantity of nickel precipitated as sulphide was seven mg; the quantity calculated from Expression 1 is five mg.

The precipitation of nickel sulphide by thioacetamide, and not by hydrogen sulphide, from acid solutions such as those described above, can be attributed to two possible causes. One of these would involve the assumption that the precipitation by thioacetamide resulted in an initial precipitate which was a less soluble form of nickel sulphide than that initially formed by hydrogen sulphide; the other would assume that the rate of the direct reaction was much faster than the rate of precipitation by hydrogen sulphide.

The above experiments with hydrogen sulphide and thioacetamide at pH 1 indicate that the precipitation by the direct reaction does not involve the formation of hydrogen sulphide. Also, Haring and Westfall[5] have reported, as was observed in this study, that nickel sulphide does not precipitate at a significant rate from solutions saturated with hydrogen sulphide at a pH of one or less. However, nickel sulphide once precipitated by hydrogen sulphide does not dissolve readily in cold 1 *VF* hydrochloric acid, and this effect is usually attributed to transformations between allotropic forms of nickel sulphide.[8]

Ringbom[7] reports that the solubility product constants of the α, β and γ forms are 3×10^{-19}, 1×10^{-24} and 2×10^{-26} respectively. At equilibrium, calculations indicate that the first form would be soluble and the last would precipitate from a solution 0.040 *VF* in nickel^{II} having a pH of 1 and saturated with hydrogen sulphide. It is possible that the γ form of nickel sulphide is formed through the direct reaction of thioacetamide with hydrated nickel^{II} and that, for this reason, precipitation was observed at a lower pH than previously reported with H_2S.

Middleton and Ward[6] suggest that the mechanism of precipitation of nickel sulphide by hydrogen sulphide involves, first, the precipitation of nickel monohydrogen sulphide, $Ni(HS)_2$, with subsequent conversion to a more insoluble nickel sulphide, NiS. If the precipitation involves a reaction between nickel^{II} and monohydrogen sulphide ion, or sulphide ion, the relatively small concentrations of these ions existing in the solutions, compared with that of the thioacetamide, could be responsible for a much slower rate of precipitation by hydrogen sulphide than by thioacetamide.

It is of interest to note that the rate constants for the precipitation by the above direct reaction of the sulphides of nickel, cadmium,[2] and lead[9] are 2.2, 8.1 and 11.5×10^{-4} litre$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ min^{-1}, respectively. The solubility product constants, as reported by Ringbom,[7] in the same order as above, are 20, 8 and 2.5×10^{-27}. Thus, for these elements the less soluble the sulphide, the more rapid is the rate of the direct reaction. More study will be needed before the validity or significance of any such correlation is established.

The separation of cadmium^{II} and lead^{II} from nickel^{II} by the use of thioacetamide

In conventional systems of qualitative analysis the Hydrogen Sulphide Group elements are separated from the remaining elements by precipitation from solutions which are saturated with hydrogen sulphide and which have hydrogen ion concentrations ranging from 0.1 to 0.3 volume molal. The sulphides of cadmium and lead are the most soluble of those precipitated and those of zinc and nickel are among the least soluble of those remaining in the solution. For this reason, and because sulphide precipitations are frequently used for quantitative separations of these elements, studies of the relative advantages of thioacetamide and hydrogen sulphide as the precipitant seemed warranted. The results from studies of the separation of cadmium and lead from nickel are presented below; the results from similar studies with zinc will be presented in a subsequent report.

Previous studies have shown that the rate of precipitation of lead[9] and cadmium[2] sulphides by thioacetamide in solutions having hydrogen ion concentrations above 0.01 is controlled by the rate of hydrolysis of the thioacetamide and that this rate is first order with respect to both the hydrogen ion and the thioacetamide concentrations. Since no evidence for the hydrolysis controlled precipitation of nickel was observed, it seemed at first that conditions were ideal for a homogeneous phase separation of lead and cadmium from nickel. However, preliminary experiments and subsequent calculations showed that there was significant precipitation of nickel by the direct reaction unless the time allowed for the precipitation and the concentrations of both thioacetamide and hydrogen ion were properly controlled.

Thus Table IV shows the data obtained from experiments with solutions at pH 2 which contained various initial quantities of nickel and of either cadmium or lead. After various times the sulphide precipitates were analyzed for nickel and the quantities found present are shown together with those calculated from the rate expression for the precipitation of nickel sulphide by the direct reaction (Expression 1). The agreement between the calculated and found quantities is in general within the accuracy of the analytical method regardless of the quantity of cadmium or lead present. This leads to the conclusion that the nickel *is not being co-precipitated but is being precipitated as sulphide by the direct reaction*, and that the rate of this reaction is not affected by the presence of lead or cadmium in the solution or of the sulphide precipitates of these elements.

A series of experiments was made to determine the extent to which under the same conditions nickel would be precipitated with cadmium and lead when hydrogen sulphide was the precipitant instead of thioacetamide. The data from these experiments are collected in Table V and they should be compared with those shown in Table IV. This comparison shows that in most cases the nickel co-precipitated by hydrogen sulphide is *relatively small* compared to that precipitated by thioacetamide under similar conditions as to pH, time, and quantity of other sulphide precipitated. These results again demonstrate the fallacy in the statement that thioacetamide can be substituted for hydrogen sulphide without change of experimental conditions.

In case one is interested in the separation of cadmium and lead from nickel by precipitation with thioacetamide it would be advantageous to work at a lower pH value than 2. Thus, since the precipitation of cadmium and lead is hydrolysis controlled, at a pH of 1 their rates of precipitation would be ten times faster than at a pH of 2 and their concentrations would be reduced to any desired concentration in one

TABLE IV.—NICKEL SULPHIDE FOUND WITH LEAD AND CADMIUM SULPHIDES PRECIPITATED AT pH 2 BY THIOACETAMIDE

Initial thioacetamide: 0.40 *VF*, Temperature: 90°, Solution volume: 10 ml.

Time, *min*	Nickel (mg) calculated[a] and found with various amounts[b] of $\mathrm{Cd^{II}}$ and $\mathrm{Pb^{II}}$				
	Calc.	Found			
		11 mg Cd	22 mg Cd	21 mg Pb	42 mg Pb
		Initial $\mathrm{nickel^{II}}$, 10 mg			
4	0.04	0.04	0.04	0.06	0.06
8	0.08	0.06	0.07	0.10	0.08
12	0.12	0.12	0.10	0.12	0.10
16	0.16	0.15	0.13	0.18	0.16
20	0.20	0.19	0.16	0.23	0.21
24	0.24	0.23	0.19	0.26	0.25
28	0.28		0.24	0.30	0.30
		Initial $\mathrm{nickel^{II}}$, 20 mg			
4	0.08	0.09		0.09	
5	0.10	0.08		0.09	
8	0.16	0.14		0.16	
10	0.20	0.18		0.18	
12	0.24	0.21		0.25	
15	0.30	0.30		0.30	
16	0.32	0.29		0.31	
20	0.40	0.42		0.39	
24	0.48	0.47		0.47	
28	0.56	0.54		0.60	
60	1.2	1.3		1.1	
90	1.6	1.5		1.5	
120	2.1	2.2		2.0	

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = 2.2 \times 10^{-4}\frac{[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}}$$

[b] Hydrogen sulphide equivalent to 11 mg Cd or 21 mg Pb formed in 12 minutes; to 22 mg Cd or 42 mg Pb in 24 minutes.

tenth the time. In addition, the rate of precipitation of the nickel by the direct reaction would be one third as fast at pH 1 as at 2. As a result of these considerations experiments similar to those above were made at pH 1 and the data are shown in Table VI. The agreement of the quantities of nickel found in the precipitates with those calculated by Expression 1 is quite striking since some precipitation may have occurred during the heating of the solutions to 90° and no correction has been made for this, also a finite "induction" period during which no nickel sulphide precipitate was observed. The agreement between the quantities calculated and found is additional evidence that the nickel is not co-precipitated, but is precipitated by the direct reaction. It is to be noted in Table V that any co-precipitation of nickel with CdS and PbS at pH 1

TABLE V.—NICKEL FOUND WITH CADMIUM AND LEAD SULPHIDES PRECIPITATED AT pH 2 BY HYDROGEN SULPHIDE

Solution saturated with H_2S. Temperature 90°. Initial nickel: 20 mg.

pH and mg Cd or Pb	Nickel, mg, found after various times				
	10 *min*	12 *min*	20 *min*	60 *min*	120 *min*
pH 2					
11 mg Cd		0.01		0.02	0.06
22 mg Cd		0.01		0.20	0.01
22 mg Cd + 42 mg Pb		0.10			<0.01
21 mg Pb		0.01			
42 mg Pb		<0.01		0.04	0.02
pH 1					
11 mg Cd	<0.01		<0.01		
21 mg Pb	<0.01		<0.01		
11 mg Cd + 21 mg Pb	<0.01		<0.01		

TABLE VI.—NICKEL SULPHIDE FOUND WITH CADMIUM AND LEAD SULPHIDES PRECIPITATED AT pH 1 BY THIOACETAMIDE

Initial thioacetamide: 0.40 *VF*, Temperature: 90°, Initial nickel$^{\mathrm{II}}$: 20 mg, Solution volume: 10 ml.

Time, *min*	Nickel, mg, calculated[a] and found with various initial amounts of Cd$^{\mathrm{II}}$ and Pb$^{\mathrm{II}}$ [b]		
	Calc.[a]	Found	
		11 mg Cd$^{\mathrm{II}}$	21 mg Pb$^{\mathrm{II}}$
2	0.01	0.02	0.02
4	0.03	0.03	0.05
5	0.03	0.04	0.04
6	0.04	0.05	0.08
8	0.05	0.07	0.11
10	0.07	0.07	0.07
12	0.09	0.14	0.15
15	0.10	0.11	0.11
20	0.13	0.15	0.15

[a] Calculated from the expression

$$-\frac{d[\mathrm{Ni^{II}}]}{dt} = 2.2 \times 10^{-4}\frac{[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]}{[\mathrm{H^+}]^{\frac{1}{2}}}$$

[b] Hydrogen sulphide equivalent to 11 mg Cd$^{\mathrm{II}}$ or 21 mg Pb$^{\mathrm{II}}$ formed in 1.2 minutes.

is less than the limit of detection of the analytical method, which, under these conditions, was 0.01 mg of nickel.

Analytical considerations

This investigation has shown that the hydrogen ion concentration and the time are both critical factors in the separation of cadmium^{II} and lead^{II}, and also other elements of the Hydrogen Sulphide Group, from nickel^{II} by sulphide precipitations from thioacetamide solutions. Calculations can be made which will permit predictions as to how effective such separations can be made. Thus if one assumes that he has 250 ml of a solution at 90° and initially 0.1 *VF* in thioacetamide and 0.10 *VM* in hydrogen ion, and containing 250 mg of cadmium^{II} and nickel^{II}, one can calculate that sulphide equivalent to the cadmium^{II} would be formed by hydrolysis of the thioacetamide within ten minutes; in this time one calculates that less than 0.25 mg of nickel sulphide would be precipitated by the direct reaction. However, the precipitation of nickel sulphide by the direct reaction will continue for as long as a significant concentration of thioacetamide remains in the solution, therefore as soon as quantitative precipitation of the cadmium sulphide is obtained one should remove the precipitate. This effect presents a serious source of trouble, especially when thioacetamide is used for analytical procedures intended for instructional purposes and where there may be intervals of days or more between periods.

A solution similar to the one above but having a pH of 2 would require almost one hundred minutes for quantitative precipitation of the cadmium^{II}. In this time over 6 mg of nickel^{II} will precipitate. Therefore, in general, such separations should be carried out at the lowest permissible pH, and in the shortest time in order to obtain maximum effectiveness of separation.

It should be noted, however, that even at a pH of 1 the amount of nickel coprecipitated when cadmium and lead sulphides are precipitated by hydrogen sulphide is smaller than that precipitated with these sulphides in comparable periods of time by the direct reaction with thioacetamide; therefore a better separation is obtained by hydrogen sulphide at this pH value. It seems reasonable that by commencing the precipitation of cadmium and/or lead sulphide by thioacetamide at lower pH values (for example with the hydrogen ion concentration 1 volume molal), and then reducing the acidity to a pH of 1 to effect their complete precipitation, the precipitation of nickel sulphide by thioacetamide may be further diminished and a much more effective separation obtained.

The above discussion has completely neglected any complex ion effects and these can seriously affect both equilibrium and rate considerations. Thus unpublished experiments in these laboratories have shown that chloride ion can have a marked inhibiting effect on the rate of precipitation of both cadmium and lead by the direct reaction. In the course of this investigation an attempt was made to use a monochloracetic acid—monochloracetate buffer but it was found that an inhibition of the direct reaction between nickel^{II} and thioacetamide resulted. This inhibition was shown not to be caused by chloride resulting from hydrolysis of the buffer.

This investigation has demonstrated the need for caution in the substitution of thioacetamide for hydrogen sulphide in analytical separations. It is hoped that further investigations will be made into other similar procedures.

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Zusammenfassung—Geschwindigkeit-messungen zeigen dass die Fällung von Nickel als Sulphid mit Thioacetamid in Lösungen von $[H^+]$ Konzentration gleich 0,3 bis 1×10^{-7} *M*, mit der Gleichung

$$-\frac{d\,[\mathrm{Ni^{II}}]}{dt} = k\,[\mathrm{Ni^{II}}]\,[\mathrm{CH_3CSNH_2}]/[\mathrm{H^+}]^{\frac{1}{2}}$$

mit k gleich $2{,}2 \times 10^{-4} L^{\frac{1}{2}}.\ Mol^{-\frac{1}{2}}.\ Min^{-1}$ bei 90° beschrieben werden können. Die Aktivations-Energie wurde im Bereich 70° bis 90° auf 20.8 Kcal/Mol berechnet. Fällung fand in Ubereinstimmung mit dierer Geschwindigkeits-Gleichung bei $[H^+]$ Konzentrationen statt, bei welchen Niederschlag mit Schweffelwasserstoffes erholten wurde. Die Wirksamkeit der Trennung von Blei(II) und Kadmium von Nickel mittels Thioacetamid in Lösungen von pH 1 bis 2 bei 90° wurde studiert. Die Bildungsgeschwindigkeit von Nickel-sulphid stimmt mit der Geschwindigkeits-Gleichung von der Konzentration von Blei, Kadmium und Schwefelwasserstoffen in der Lösung unabhängig. Die Menge von Nickel-sulphid gefällt mit Kadmium- und Blei-sulphid in Folge einer direkten Reaktion zwischen Nickel und Thioacetamid übertrifft die mitgefällte Menge im Falle der Kadmium und Blei-Fällung mit Schwefelwasserstoff. Unter optimalen Bedingungen sind aber Trennungen möglich.

Résumé—La précipitation du nickel^{II} de ses solutions à l'état de sulfure par la thioacétamide dans un grand domaine de pH répond à une expression, dérivée de mesures de vitesse, qui n'implique pas une précipitation controlée par l'hydrolyse; cette précipitation a lieu à des concentrations d'ions hydrogènes auxquelles on n'obtient pas de précipitation par l'hydrogène sulfuré.

L'efficacité de la séparation du plomb^{II} et du cadmium^{II} d'une part et du nickel^{II} d'autre part, par l'emploi de thioacétamide en solutions de pH 1 et 2 maintenues à 90°C a été étudiée. La vitesse de formation du sulfure de nickel est conforme à l'expression dérivée de la vitesse et est indépendante de la quantité de sulfure métallique présent ainsi que de lac oncentration du plomb^{II}, du cadmium^{II} et de l'hydrogène sulfuré dans la solution. La quantité de sulfure de nickel précipitée avec les sulfures de cadmium et de plomb par réaction directe entre l'ion nickel et la thioacétamide dépasse celle ayant co-précipitée quand le cadmium et le plomb sont précipités par l'hydrogène sulfuré. Cependant dans des conditions correctement contrôlées on peut obtenir une séparation effective.

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TITRIMETRIC DETERMINATION OF TETRAPHENYLBORON BY THALLIUM^{I}

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Summary—A titrimetric procedure for the determination of sodium tetraphenylboron, based upon its precipitation by a known excess of thallium^{I} and back-titration of the excess with standard potassium iodate, is described.

INTRODUCTION

EARLIER work from these Laboratories[1] employing high-frequency technique for the detection of end-points has shown that thallium^{I} and silver form sparingly soluble tetraphenylborates of the composition $Tl(C_6H_5)_4B$ and $Ag(C_6H_5)_4B$ respectively. Using these it was possible to determine small quantities of thallium, silver, or tetraphenylboron (TPB) in comparatively high dilutions.

Since its discovery by Wittig and co-workers[2] in 1949, sodium tetraphenylboron has been employed as a precipitating reagent for K^+, Rb^+, Cs^+, Tl^+, and NH_4^+ and several organic nitrogen compounds.[3] In all these procedures, excess of the reagent is always used and it is therefore not necessary to know the exact strength of NaTPB. While tetraphenylborates are usually analysed gravimetrically, titrimetric approaches, particularly for potassium, such as ignition of KTPB and titration of the resulting metaborate with standard acid[4,5] and argentometric titration of KTPB dissolved in acetone using an indicator[6] or amperometric[7] end-point, have also been described. The knowledge of exact strength of NaTPB is important when stoichiometric studies are made by a direct titration. This could be done by either weighing the sample of known purity or standardizing by a suitable method. Since little information is available in the literature, it was thought desirable to develop a rapid and reliable method for standardization. The present communication reports a titrimetric procedure, based on the quantitative precipitation of TPB ion by a known excess of thallium^{1} solution and titrating the excess with standard potassium iodate.

EXPERIMENTAL

An analytically pure sample (99.8% assay) of NaTPB, supplied by J. T. Baker Chemical Company, was used in the present work. The given assay is based on the procedure of Flaschka and co-workers originally developed for the determination of potassium.[8] Mercuric chloride is added to an acetone solution of TPB in presence of an excess of standard alkali and the excess is back-titrated with a standard acid.

A standard solution of KIO_3 was prepared by direct weighing of the pure sample after drying it at 160–180° for 2–3 hours. Thallium^{I} nitrate solution was standardized by titration in 3*N*–4*N* hydrochloric acid solution with iodate to the iodine monochloride end point using chloroform as indicator. The following procedure was adopted for the determination of tetraphenylboron:

Procedure

An aliquot portion of NaTPB solution was precipitated by a known excess of thallium^{I} nitrate. After standing 4–6 hours, the precipitate was filtered through Whatman No. 42, washed 8–10 times with about 10 ml of water, and the unused thallium$^{\mathrm{I}}$ in the filtrate was titrated with standard KIO_3 in presence of hydrochloric acid as described above. The difference in the two titers of iodate corresponds to the weight of NaTPB present originally:

$$\mathrm{NaTPB} + \mathrm{TlNO_3} \rightarrow \mathrm{TlTPB} + \mathrm{NaNO_3}$$

$$2\mathrm{TlNO_3} + \mathrm{KIO_3} + 8\mathrm{HCl} \rightarrow 2\mathrm{TlCl_3} + \mathrm{KCl} + \mathrm{ICl} + 2\mathrm{HNO_3} + 3\mathrm{H_2O}$$

Thus 1 ml of 1 M-KIO_3 is equivalent to 0.68447 g of NaTPB. Results of a representative set of experiments are entered in Table I.

TABLE I. DETERMINATION OF TETRAPHENYLBORON BY THALLIUM$^{\mathrm{I}}$

NaTPB, *g*		Difference, *g*
Calculated	Found	
0.03480	0.03470	0.0001
0.06865	0.06852	0.00013
0.06960	0.06940	0.0002
0.1044	0.1041	0.0003
0.1392	0.1388	0.0004
0.1740	0.1735	0.0005

It will be seen from Table I that the weight of NaTPB obtained experimentally is in fair agreement with that taken actually. Besides, the present method is simple and rapid with the additional advantage of using KIO_3 as a primary standard. A series of experiments performed by the described method showed that the TPB content, corresponding to what may be termed as the "precipitating power," of a given NaTPB solution remains unaltered for a period of seven days if the solution is stored in refrigerator. At room temperature (30°) and in ordinary daylight, the solution decreases in its strength after about 48 hours.

Acknowledgement—We are indebted to Boyd Professor Philip W. West for research facilities and interest in the work. Grateful thanks are also due to Dr. A. J. Barnard, Jr., J. T. Baker Chemical Company, Phillipsburg, for valuable discussions.

Zusammenfassung—Es wurde ein titrimetrisches Verfahren zur Bestimmung von Natrium-tetraphenylbor durch Fällung mit einem Überschuss von Thallium(I) und Ruck-titrieren des Überschusses mittels Standard-Kalium-jodat beschrieben.

Résumé—Les auteurs décrivent une méthode volumétrique pour le dosage du tétraphenylborure de sodium, basée sur sa précipitation par un excès connu de thallium$^{\mathrm{I}}$ et le dosage en retour de l'excès par de l'iodate de potassium titré.

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EARLY PREPARATION AND ANALYTICAL USE OF HYDROGEN SULPHIDE

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Summary—Robert Boyle obtained hydrogen sulphide and applied it as an analytical reagent in 1685 for the detection of mercury, tin, lead and copper.

THE "sulphur-liver" test has been known for a long time. Treated with acids hydrogen sulphide is developed. Even the alchemists must have met this phenomenon but, having no knowledge about gases at that time, they probably paid no attention to it. According to Kopp[1] it was F. Hoffman[2] who first mentioned hydrogen sulphide, writing about a gas smelling of rotten eggs and obtained by the acidification of caustic sulphur solutions. Hydrogen sulphide was more fully studied by Rouelle[3] in 1774. It was stated by Bergman,[4] that hydrogen sulphide water gave precipitates of different colour with many metal-salt solutions. These reactions were fully studied by him. It is interesting that this great analyst did not think of the analytical utilization of these reactions. Until now it has been held in the literature that Fourcroy[5], and at the same time Hahnemann,[6] both recommended hydrogen sulphide as an analytical reagent for the detection of lead. Robert Boyle, however, long before that, obtained hydrogen sulphide and applied it as analytical reagent. This appears from his *Memoirs for a Natural History of Mineral Waters* published in 1685.

Dealing with the use of the long known metal-reagent, tincture of galls, he states that its use is not so certain as it is believed to be. Some of the metals in water, like arsenic or lead may not give a colour with it. "But, probably, the sulphureous spirit we shall presently describe, wou'd have shewn that water to be impregnated with a body of the nature of vitriol, but not the common sort. For the' galls give no very blackish colour to a solution of Sacharum Saturni, that is, the vitriol of lead, in distill'd or rain-water yet I found this volatile sulphur wou'd soon manifestly do it: which expedient I made use of, because I had not then at hand the ores of lead, copper, etc. For the same reason I contented myself with the solutions of the several metals in their proper menstrua; for 'tis probable, that the metalline parts of the ores, wou'd have afforded either the same, or similar solutions, in the same menstrua; which consisting of nitre, sea-salt, and vitriol, bodies that abound in several parts of the earth thro' which springs flow, their several impregnated waters might exhibit phenomena of the same kind. We made then, among others, a solution of fine gold in Aqua regis; another of common running mercury in Aqua fortis; and a clear one of tin, in a peculiar solvent that readily acts upon it, and keeps it permanently dissolv'd. To these solutions I put galls, without obtaining any blackish colour, except from that which contained gold; but with our sulphureous liquor, we obtained notable changes of colour, tho' 'twas dark in all of them, except one, or tending to blackness. And tho' for that reason a careless eye might judge them indifferently blackish, yet, since the degrees, or some other modification of the same dark colour, seemed plainly not to be the same in them all; 'tis possible, that a very careful view may discern some little differences between those obscure colours, from whence to form a conjecture, what metalline substance is contained, or at least predominates in the respective liquors. And I particularly remember, that the colour which arose from our sulphureous liquor, and the solution of tin, was manifestly distinguishable from those produced in any of the other solutions; being not black or blackish, nor so much as purple; but of a kind of brownish yellow."[7]

Later Boyle also describes the production of the "sulphureous spirit": "... take equal parts of pure salt of tartar (K_2CO_3), flowers of sulphur, and good sal-ammoniac (NH_4Cl), reduce the first and the last to powder separately, melt the sulphur, over a gentle fire, and, by degrees, put to it the salt of tartar; stirring them well, that they may incorporate and grow reddish; then put the mixture, pulverized, into a glass-retort, pour on it the sal-ammoniac dissolv'd in fair water; and closing well the junctures, distil all in sand, by degrees of a moderate fire; shifting the receiver once or twice, because the liquors will be differently ting'd and strong, and that which ascends last, may bring over but very little of the sulphur, whose volatile tincture is yet the chief thing we aim at in this operation."[8]

Repeating Boyle's experiment I have found that hydrogen sulphide is in fact developed.

Boyle also used his reagent for the detection of copper: "... yet common English vitriol, as also that of Dantzick, which is of the copper kind, will presently turn it of a black or very dark colour."[9]

But it is worth observing that he did not get any precipitate with arsenic: "... and to another portion of the same liquor (arsenic) we put some of our volatile sulphureous spirit, but no precipitation ensued."[10] The solution was probably alkaline.

Zusammenfassung—Robert Boyle erzeugte schon im Jahre 1685 Schwefelwasserstoff und benützte es bei Wasseranalysen zum Nachweis von Quecksilber, Zinn, Blei und Kupfer.

Résumé—Robert Boyle a préparé de l'acide sulfhydrique et l'a utilisé comme réactif analytique en 1685 pour la caractérisation du mercure, étain, plomb et cuivre.

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POLAROGRAPHIC EXAMINATION OF THE CHELATING POWER OF EDTA AND SOME CLOSELY RELATED CHELATING AGENTS*

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A rapid polarographic method has been devised for assessing the chelating power of new reagents of the complexone type and for comparing such reagents with complexones of known stability. A standard chelate scale based on Cu^{II} chelates has been set up. A linear relationship appears to exist between $\Delta E_{\frac{1}{2}}$ and Log K for known complexones, but this may not hold for newer complexones which are considerably more powerful in their cation binding powers.

IN the course of an investigation into the properties of some homologues of ethylenediaminetetra-acetic acid (EDTA) and other aminopolycarboxylic acids it was found necessary to evolve a rapid method for estimating the chelating power of these reagents.

It is well known that the polarographic wave for the aquo-ion complex of simple metal cations is shifted towards more negative potentials when the ion enters into chelate formation. There are several methods available for relating the induced shift in the half-wave potential to the instability constant of the chelate thus formed. These have been reviewed recently by Rossotti.[1] The most attractive of these methods appeared to be that in which the half-wave potential of the chelate wave is measured in the presence of varying excesses of the reagent. It is then only necessary to know the dissociation constant of the chelating acid and its concentration in order to calculate the desired $\log_{10} K$ value. Unfortunately the aqueous solubility of EDTA and similar reagents is sufficiently low to preclude the use of this method and moreover the waves do not appear to be fully reversible. It was therefore decided to establish a standard curve relating experimentally observed $E_{\frac{1}{2}}$ values to the known chelation constants of a selected cation with various reagents and to use this as a means of estimating unknown K values for new reagents.

This method has the advantage of extreme rapidity and simplicity and it requires very little material.

In setting up such a chelate scale several factors must be considered in selecting a suitable cation.

(1) A low pH must be used to decrease the stability of the chelate.

(2) The cation itself must have a low $E_{\frac{1}{2}}$ value in order to give as wide a working range as possible between $E_{\frac{1}{2}}$ for the unchelated cation and the hydrogen wave.

(3) The cation should preferably give only one wave.

(4) The cation should be such that it allows a reasonable movement of $E_{\frac{1}{2}}$ on chelation with a strong reagent without the wave merging with that of hydrogen.

(5) The chelate formed with the weaker chelating agents, *e.g.* iminodiacetic acid, must be sufficiently stable not to break down at the selected pH.

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* This paper was presented in part at a meeting of the Polarographic Society, held at Nobel Division, Imperial Chemical Industries Ltd., Stevenston, Ayrshire, on 26 September 1958.

Zinc, nickel and cobalt give no chelate waves with EDTA at pH > 2.7 (*i.e.* the waves lie beyond the H_2 wave); thallium,^{I} arsenic^{III} and molybdenum^{VI} do not fulfil condition (4); chromium^{III} and tin^{II} are also not suitable (Condition 3)^2. Of the remaining common cations copper^{II} and cadmium were selected for further investigation.

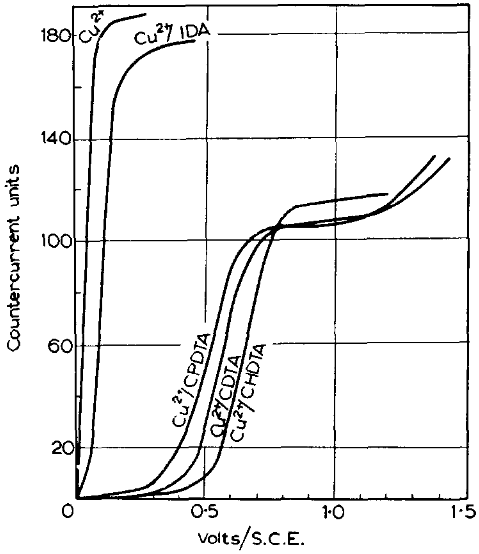

FIG. 1.

INVESTIGATION OF CU^{II} CHELATES

The half wave potential of the Cu^{2+}/EDTA chelate depends on several factors, *e.g.* pH, ionic strength, temperature, concentration of chelate, excess of chelating agent, concentration of buffer, etc. These variables all require control, but the most important single factor is the first mentioned.

At pH 4.6, weak chelating agents such as iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), etc., give a single chelate wave as do very strong chelating agents such as 1:2-diamino*cyclo*hexane-N:N:N′:N′-tetra-acetic acid (CDTA), *cf.* Fig. 1.* However, chelating agents of intermediate strength, *e.g.* EDTA give double waves and sometimes even more complex behaviour, *cf.* Fig. 2.

In 0.4*M* acetic acid all chelating agents examined were found to give a single wave which required the use of a maximum suppressing agent, *cf.* Fig. 3. Gelatin appeared to be the most effective of these. However, the concentration of gelatin has a considerable effect on the $E_{\frac{1}{2}}$ values for the chelate wave, *i.e.* $E_{\frac{1}{2}}$ is found to increase with gelatin concentration. Of other suppressing agents examined, only "Cetavalon" was successful, but it showed some disturbing effects on the relative order of chelation as related to $E_{\frac{1}{2}}$ values, and like gelatin, its concentration had a pronounced effect. The choice of maximum suppressing agent was therefore restricted to gelatin. It was noted that the greater the stability of the chelate, the lower the concentration of gelatin necessary to suppress the maximum. A final concentration of 0.025% was

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* The data in Figs. 1–3 were obtained in early experiments with a Cambridge manual polarograph.

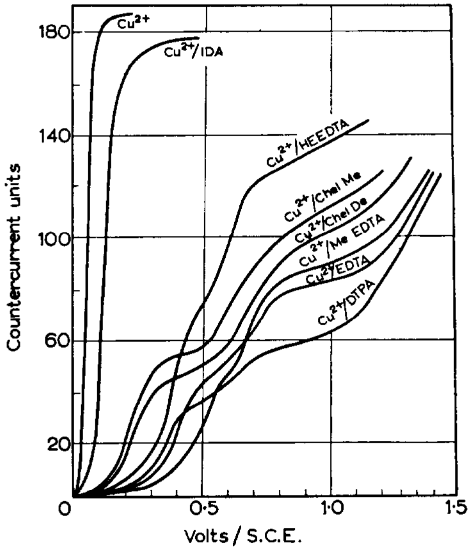

FIG. 2.

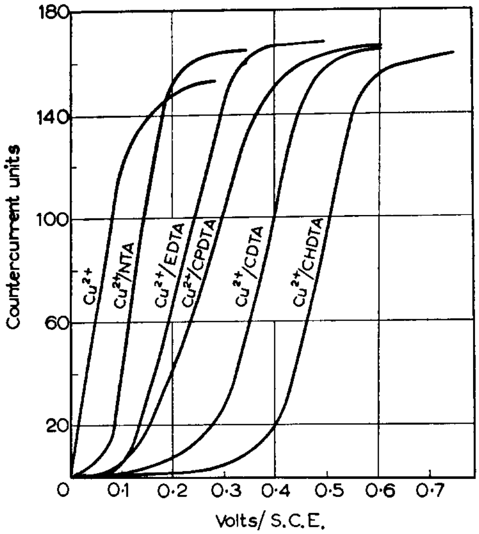

FIG. 3.

chosen as this was the minimum required for suppressing maxima obtained with the weaker reagents such as NTA.

When the optimum conditions for this and other factors had been established, the $E_{\frac{1}{2}}$ values were determined for a number of copper chelates of known stability. Since a stability constant cannot readily be assigned to the copper^{II} aquo-ion complex, in an acetate medium, and since it is certainly not zero, the cupric chelate of di-(2 hydroxyethyl) glycine (DHEG) with $E_{\frac{1}{2}} = -0.02$ and $\log_{10} K = 8.1$ was chosen as arbitrary (zero) reference point, and a standard curve relating observed $\Delta E_{\frac{1}{2}}$ values* to known

* $\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}(\mathrm{Chelate})} - E_{\frac{1}{2}(\mathrm{DHEG})}$

$\Delta \log_{10}$ K values[3] was established *cf.* Fig. 4. The curve was extrapolated beyond the plot for CDTA to enable us to assess the stability of new reagents which form more stable chelates than CDTA (previously the strongest known). The true shape of the curve beyond this point will become apparent when the instability constants for the new reagents have been determined.

About 20 aminopolycarboxylic acids of the "complexone" type were investigated in setting up this standard curve, *cf.* Table I. A list of estimated instability constants for some new chelating agents has been established as a result of this work, *cf.* Table II. Certain complexones, *e.g.* CHEL DE, which have extra co-ordinating centres do not fall on the curve. We presume that such reagents form protonated species for which data are not available.

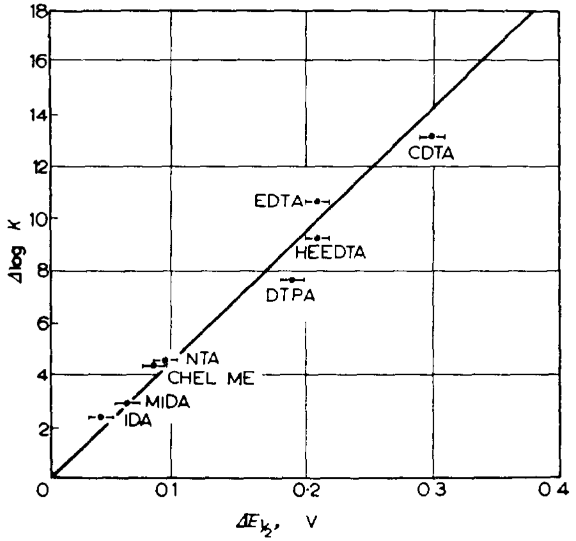

Fig. 4.

A number of chelating agents showed unusual "reversed current" behaviour at the dropping mercury electrode. During the early stages of reduction, *i.e.* before the $E_{\frac{1}{2}}$ point on the polarogram, these chelates behaved in such a way that the current was observed to decrease as the drop size increased and to increase immediately the drop fell off. However, at a more cathodic potential, but before the limiting current was reached, the normal pattern of behaviour was observed *viz* increase of current up to maximum drop size. The point of change over was indicated by a sharp kink in the polarogram, *cf.* Fig. 5.

This phenomenon is probably associated with the gelatin coverage of the surface of the mercury drop. Under certain circumstances the coverage of the mercury surface by gelatin is known to increase as the drop surface advances out into the liquid.[4] Consequently, during its life-time the mercury drop becomes increasingly protected against the phenomenon which causes the formation of maxima so that as the drop grows the current falls of to a minimum at maximum drop size and increases sharply as soon as the new drop begins to form. During the early stages of reduction, *i.e.* before the $E_{\frac{1}{2}}$ value for the polarogram has been attained, the electrode reaction is relatively slow and so this phenomenon is observed, but at more cathodic potentials

TABLE I. CATHODIC HALF-WAVE POTENTIALS FOR THE POLAROGRAMS OF VARIOUS CHELATES AT pH 2.5

Chelate	$E_{\frac{1}{2}}$		Chelate	$E_{\frac{1}{2}}$	
	Cu^{2+}	Cd^{2+}		Cu^{2+}	Cd^{2+}
D.H.E.G.	0.02		Chel. 138	0.16	
I.D.A.	0.06	0.60	D.T.P.A.	0.21	
M.I.D.A.	0.08		H.E.E.D.T.A.	0.23	
A.A.D.A.	0.08		E.D.T.A.	0.23	0.82
Chel. ME.	0.10		C.P.D.T.A.	0.24	0.93
Chel. DE.	0.11		M.E.D.T.A.	0.29	0.88
D.P.T.A.	0.11		C.D.T.A.	0.32	1.04
N.T.A.	0.11	0.60	2 : 3 B.D.T.A.	0.41	0.97
U.D.A.	0.16		C.H.D.T.A.	0.42	1.08

Abbreviations:

M.I.D.A. Methyliminodiacetic acid.
A.A.D.A. *o*-Carboxyphenyliminodiacetic acid.
U.D.A. Uramil-N:N-diacetic acid.
M.E.D.T.A. 1:2-Propylenediamine-N:N:N′:N′-tetra-acetic acid.
* Chel. ME. 2:2′-Bis[di(carboxymethyl)amino]diethyl ether.
* Chel. DE. 1:2-Bis-[2-di(carboxymethyl)aminoethoxy] ethane
* D.P.T.A. 1:3 Diaminopropan-2-ol-N:N:N′:N′-tetra-acetic acid.
* Chel. 138 N:N′-Ethylene bis [2-(*o*-hydroxyphenyl)] glycine.
D.T.P.A. Diethylene triamine-N:N:N′:N″:N″-penta acetic acid.
* H.E.E.D.T.A. N-(2-Hydroxyethyl) ethylene diamine-N:N′:N′-tri acetic acid.
† C.P.D.T.A. *trans*-1:2-Diaminocyclopentane-N:N:N′:N′-tetra-acetic acid.
† C.H.D.T.A. 1:2-Diaminocycloheptane-N:N:N′:N′-tetra-acetic acid.
† 2:3 B.D.T.A. 2:3-Diaminobutane-N:N:N′:N′-tetra-acetic acid.

* Supplied by The Geigy Co. Ltd.
† Synthesised by the authors.[6]

TABLE II.—STABILITY OF CHELATES BY THE POLAROGRAPHIC METHOD

Cu^{2+} Chelate	Estimated log K
U.D.A.	15
A.A.D.A.	11
C.P.D.T.A.	19
M.E.D.T.A.	21
2 : 3 B.D.T.A.	>22
C.H.D.T.A.	>22

the reduction process speeds up and the electrode reaction then becomes diffusion controlled so that the effect of the gelatin coverage of the drop surface is no longer observed. Where such polarograms were encountered, current measurements were made on the part of the curve corresponding to maximum *drop* size.

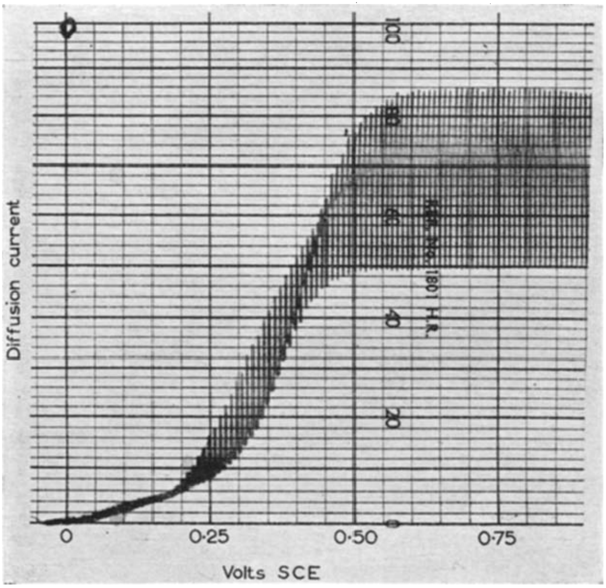
Diffusion current
100
80
60
40
20
0
1801 H.R.
0
0·25
0·50
0·75
Volts SCE

FIG. 5

INVESTIGATION OF CADMIUM CHELATES

Cadmium is less satisfactory than copper for the purpose of setting up a chelate scale because of the lower stability of the chelates of this cation and the more cathodic value of the $E_{\frac{1}{2}}$ value for the unchelated ion. Thus weak chelating agents which yield quite satisfactory chelates waves with Cu^{II} show no such wave with Cd^{2+}, whilst the polarogram for strong chelating agents is situated too close to the hydrogen wave to permit accurate measurements. The Cd^{2+}/EDTA polarogram (pH 2.5) shows two waves, the first of which corresponds to free cadmium ion and the second to the Cd^{2+} chelate. Whilst this work was in progress a similar observation was reported by Schmid and Reilley[5] in the U.S.A.

We have determined the polarograms of a range of the more powerful chelating agents with cadmium in 0.4*M* acetic acid at pH 2.5 without the use of a maximum suppressing agent. Most of these polarograms show twin waves, but the more powerful the chelating agent the smaller was the wave due to free cadmium till eventually for reagents such as CDTA (and some of the yet more powerful chelating agents which we have devised) no free cadmium could be observed. At the same time, the half-wave potential of the second wave became more negative and for the more powerful reagents it eventually became difficult to determine $E_{\frac{1}{2}}$ because the diffusion current of the chelate merged with the start of the hydrogen wave.

A Cd^{2+} chelate scale corresponding to the Cu^{II} scale was not set up as sufficient data are not available. Only the relative strengths of the chelates were determined. These show some slight divergence from the order obtained with Cu^{II}, but this is not entirely unexpected.

CONCLUSIONS

As a result of the evolution of this rapid method for the estimation of the chelating ability of new reagents on quite minute amounts of material, it was possible to obtain fairly precise data on the chelating power of new reagents in a matter of a few hours rather than the days it would have taken by more customary methods. Furthermore less precise data could sometimes be obtained on the reaction mixture itself without having recourse to the extremely tedious procedures which are usually necessary for the isolation of some of the aminopolycarboxylic acids.

EXPERIMENTAL

Reagents

Copper sulphate solution: 0.002*M* in 0.4*M* acetic acid containing 0.025% of gelatin, freshly prepared before use, pH 2.5.

Complexones: 0.1*M* aqueous solutions of the sodium salts.

Cadmium sulphate solution: 0.001*M* solution in 0.4*M* acetic acid, pH 2.5.

Apparatus

Tinsley Recording Polarograph Mark 19, with dropping mercury electrode (drop time 5.2 sec, under an open head of mercury of 37 cm) and a saturated calomel electrode with a potassium chloride bridge as a reference electrode. E.I.L. Direct Reading pH Meter.

The polarographic determination of chelate stability

To 10 ml of the copper sulphate solution in a 20-ml beaker, 0.3 ml of the complexone solution was added. The pH of the solution was measured, and adjusted where necessary to pH 2.5 with concentrated hydrochloric acid or sodium hydroxide solution. After the solution had been deoxygenated with hydrgoen an undamped polarogram was recorded using a sensitivity of 12 μA, no counter current, and a chart scale of 1 volt/4″. All the determinations were done at room temperature. The half-wave potentials were measured to within ±10 mV, from the curve drawn through the points given by the current at maximum drop size.

The polarographic examination of some cadmium chelates

To 10 ml of the cadmium sulphate solution, 0.2 ml of the complexone solution was added. The pH of the solution was checked to be 2.5, and a polarogram determined after deoxygenation at a sensitivity of 7.5 μA, with no damping, a counter current of 2 or 3, and a chart scale of 1 volt/4″. The determinations were done at room temperature. The half-wave potentials were measured as above.

Acknowledgements—We are grateful to The Geigy Co. Ltd. for the provision of a research grant to one of us in aid of this work, and to Dr. R. Belcher for his interest and helpful advice.

Zusammenfassung—Aus der polarographischen Untersuchung der Reihe von Kupfer- und Kadmium-Chelate mit grossen Anzahl der Komplexon-Art-Verbindungen wurde eine Methode zur raschen Bestimmung des Chelat-Vermögens eines neuen Reagens entwickelt.

Résumé—On a imaginé une méthode pour l'analyse rapide du pouvoir complexant d'un noveau réactif à partir d'une étude polarographique des complexes du cuivre et du cadmium, avec une large série de composés du type "complexon".

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QUANTITATIVE EVALUATION OF CHROMATOGRAMS BY DOUBLE DECOMPOSITION WITH SIMPLE RADIOACTIVE REAGENTS—I

THE USE OF $Ag^{131}I$ IN RADIOMETRIC ESTIMATION OF ORGANIC AND PHOSPHORIC ACIDS

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Summary—A method which it is proposed to call "double decomposition radiochromatography" has been developed for the radiometric estimation of saturated fatty acids, inorganic phosphates and glucose-1-phosphates on paper chromatograms, by forming insoluble silver salts on the paper strip, followed by decomposition of the salt with ^{131}I-iodide, and radiometry of the $Ag^{131}I$ deposit. Integrated activities of spots are linearly related to spot content. The maximal (peak) spot activity is proportional to the logarithm of spot content for fatty acids and phosphates, but not for glucose-1-phosphate.

IN a previous publication[1] the authors have shown that saturated fatty acids could be estimated after paper chromatographic separation, by forming insoluble silver soaps on the strip, followed by decomposition of the soaps with radioactive iodide to form localized precipitates of $Ag^{131}I$, corresponding in geometry to the fatty acid spots. In general it would seem that this method could be applied in all cases where the chromatographically separated substances can form insoluble local precipitates on the strip with a cation or anion, which in turn by double decomposition can form a second insoluble precipitate with an appropriate radioactive anion or cation. In this way, by using simple precipitation reactions, it might be possible to label chromatograms for quantitative radiometric estimation, with easily available active anions or cations, without the necessity for preparing specially labelled, more complex reagents for attaching the tracer to the chromatographed material.

In the case of silver soaps decomposed with $^{131}I^-$, it was shown that reproducible relationships could be established between spot content and such parameters as radiometrically defined spot length or peak spot activity. These relationships were adequate for estimating content of substance in the spot. Such parameters can be adequately estimated by means of radioactive labelling, even if the labelling agent is not stoichiometrically bound to the spot. This fact gives wider possibilities of application to the method which we propose to call "double decomposition radiochromatography".

Silver ion forms precipitates of sufficient degree of insolubility for localization on the chromatogram with a number of anions, and all these precipitates will in turn undergo double decomposition with I^-, in view of the exceptional insolubility of AgI. This paper deals with the use of $Ag^{131}I$ in the radiometrical analysis of chromatograms of organic acids, phosphoric acids, and an ester of phosphoric acid, all of which give adequately insoluble silver salts.

In all cases where the labelling isotope has a β-particle energy sufficiently high to render counting efficiency practically independent of fluctuations of paper thickness, radiometric methods for estimating chromatograms will be superior to the photometry of coloured spots on strip, which is liable to considerable error due to variation of strip thickness. Thus methods which simplify labelling of chromatograms could receive wide application.

EXPERIMENTAL

The following compounds were chromatographed:

(a) lauric, myristic, palmitic and stearic acids as representatives of carboxylic acids,

(b) orthophosphate, pyrophosphate, trimetaphosphate and hypophosphate as representatives of phosphates,

(c) glucose-1-phosphate as representative of phosphoric acid esters.

The carboxylic acids were separated by reversed-phase chromatography on Schleicher and Schüll 598 L paper strips of 15 mm width and 280 mm length by a previously described method[2], using a mixture of synthetic hydrocarbons of very low bromine number (0·16), and boiling point 180–190° C., called 'Mepasine' (Polish product, Ciech, Warsaw), as stationary phase, and 90 per acetic acid saturated with 'Mepasine' as mobile phase in ascending reversed phase chromatography under nitrogen. 'Mepasine' is applied to the strips as a 20 per cent solution in freshly distilled ether free of peroxide, followed by evaporation of the ether. Phosphates and phosphate ester were chromatographed by the method of Ebel and Volmar[3] on Whatman No. 4 paper.

After chromatography the strips were dried in air and then immersed in narrow vessels made of paraffin wax of minimal volume to immerse the freely hanging strips fully, for subsequent operations. Fifteen ml of a saturated solution of silver acetate were poured into the vessels, and served to cover the chromatograms. After 15 minutes this solution was decanted and the chromatograms then washed three times for five minutes each with water. After decanting the final portion of water, there was added 15 ml of solution $0{\cdot}01M$ in potassium iodide, and containing about 3 μC $K^{131}I$ per ml. After 15 minutes immersion, the active solution was removed, and the chromatograms washed three times for five minutes with water, and then removed from the vessels, and allowed to dry in the dark at room temperature.

Activity measurements were made with a previously described apparatus[1] using a 2-mm slit width.

RESULTS AND DISCUSSION

The results are shown in Figs. 1–6.

Figs. 1–3 show the relationship between spot content and integrated spot activity (as previously defined[1]). As can be seen, in all cases a linear relationship is obtained suitable for estimation of spot content within a useful range of amounts of chromatographed substance. In our hands average errors for determination of the organic acids lie in the range 4·6–7·1% for 50–400 μg of chromatographed substance, 4·9–11·2% for the phosphoric acid ions for 50–500 μg of chromatographed substance, and 1·9% for glucose-1-phosphate for 20–300 μg of chromatographed substance. These errors must be considered quite satisfactory for quantitative evaluation of radiochromatograms.

Figs. 4–6 show the relationship between spot content and maximal spot activity (as previously defined[1]). Figs. 4 and 5 show that for saturated fatty acids and phosphates a satisfactory linear relationship is obtained between maximum spot activity and logarithm of spot content. On the other hand an inverse relationship appears to prevail for glucose-1-phosphate, as shown in Fig. 6. where the logarithm of maximal activity seems rather to be proportional to spot content.

The average error for determination of the chromatographed substances using

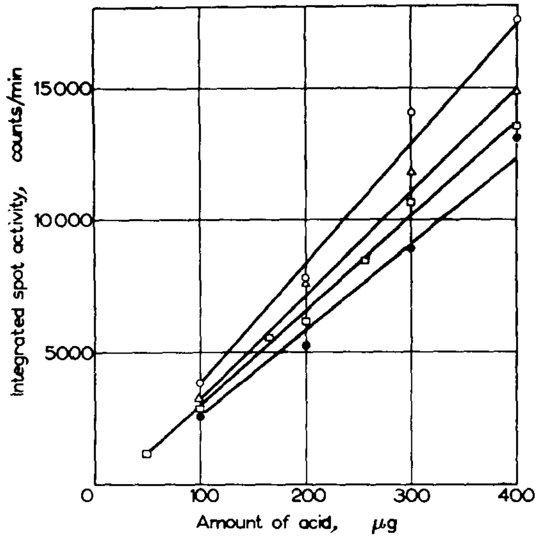

FIG. 1. Relationship between integrated spot activity and spot content for saturated fatty acids after decomposition of the silver soaps with $^{131}I^-$; ○ lauric acid, △ myristic acid, ☐ palmitic acid, ● stearic acid.

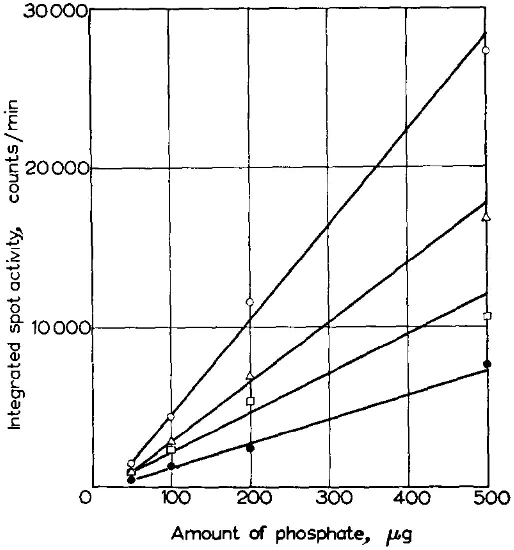

FIG. 2. Relationship between integrated spot activity and spot content for phosphates after decomposition of the silver salts with $^{131}I^-$; ○ Na_2HPO_4, △ $K_4P_2O_6$, ☐ $K_4P_2O_7$ ● $Na_3(PO_3)_3$.

the relationships between maximal spot activity and spot content as shown in Figs. 4–6, was less than 8·5% for all the substances examined. This error is also satisfactory for quantitative chromatographic analysis. Where the components of a mixture are well separated on a chromatogram it will be better to use the relationship between integrated spot activity and spot content for quantitation, but if peaks are crowded together and overlap it may sometimes be difficult to evaluate the peak

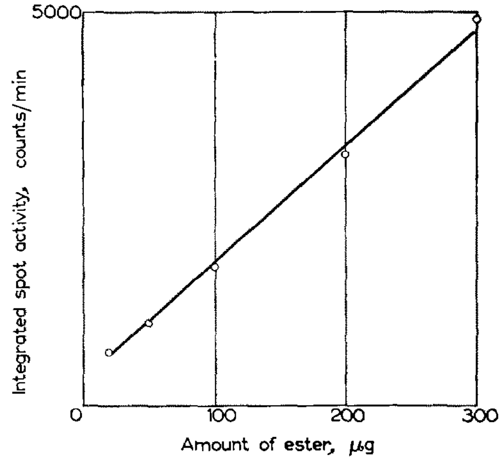

Fig. 3. Relationship between integrated spot activity and spot content for glucose-1-phosphate after decomposition of the silver salt with $^{131}I^-$.

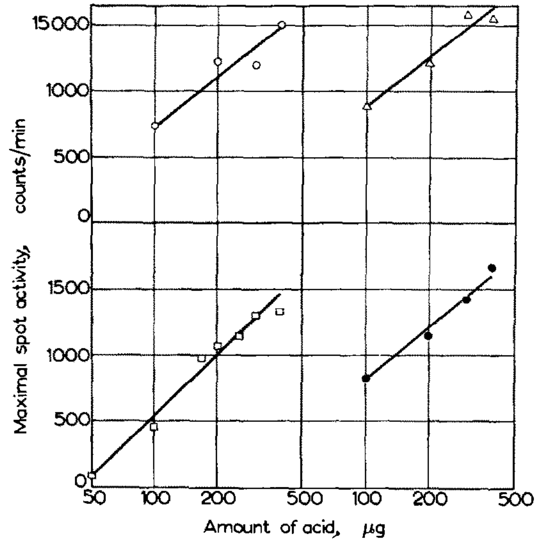

Fig. 4. Relationship between maximal spot activity and logarithm of spot content for saturated fatty acids after decomposition of the silver soaps with $^{131}I^-$; ○ lauric acid, △ myristic acid, □ palmitic acid, ● stearic acid.

area, and in this case the relationship between maximal spot height and spot content can be very useful.

In all cases examined, except palmitic and stearic acids, no satisfactory linear or logarithmic relationship was found between spot content and radiometrically defined spot length, contrary to the situation found previously[4] with chromatograms of unsaturated fatty acids iodinated with ^{131}I.

For purposes of quantitative estimation it is necessary to set up calibration curves based on chromatograms of known amounts of pure substances alongside the chromatogram of the mixture being analysed, to allow for given chromatographic conditions.

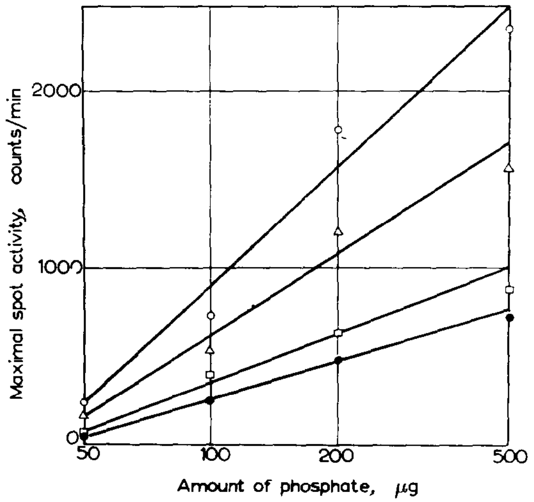

FIG. 5. Relationship between maximal spot activity and logarithm of spot content for phosphates after decomposition of the silver salts with $^{131}I^-$; ○ Na_2HPO_4, △ $K_4P_2O_6$, □ $K_4P_2O_7$, ● $Na_3(PO_3)_3$.

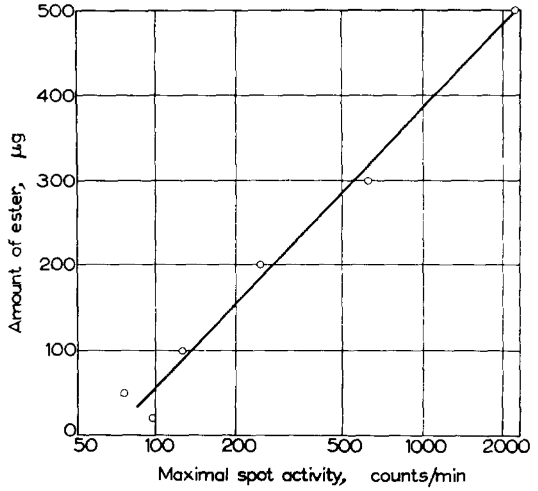

FIG. 6. Relationship between spot content and logarithm of maximal spot activity for glucose-1-phosphate after decomposition of the silver salt with $^{131}I^-$.

From the above results together with previous results[1] it can be seen that integrated spot activity is proportional to spot content after decomposition of silver salts with $^{131}I^-$ for fatty acids, phosphates and a phosphate ester. The maintenance of such a relationship for different substances suggests that in all examples studied, the silver salts are quantitatively formed on the chromatograms, and quantitatively decomposed by the $^{131}I^-$, without significant losses from the paper during washing.

In the case of the saturated fatty acids and phosphates, the linear relationship between maximum spot activity and logarithm of spot content previously found[4] for unsaturated fatty acids iodinated with ^{131}I, is satisfactorily maintained. This suggests that such a logarithmic relationship between maximum thickness of spot and spot content may be widely applicable in paper chromatography, although the occurrence of an inverse relationship for glucose-1-phosphate shows that the phenomenon is not entirely general.

Failure to find a satisfactory linear relationship between radiometrically defined spot length and spot content for the substances here examined, indicates that the maintenance of such a relationship for unsaturated acids iodinated with ^{131}I as previously reported[4] is probably of limited significance.

The present work shows that double decomposition radio-chromatography with $Ag^{131}I$ can be used for estimation of chemically different substances capable of forming insoluble salts with silver on the chromatogram.

Zusammenfassung—Es wird eine Methode "Doppel-Zersetzung-Radiochromatographie" genant zur radiometrischen Bestimmung von gesättigen Fettsäuren, anorganischen Phosphaten und Glykose-1-phosphaten auf Papier-chromatogrammen durch Bildung von unlöslichen Silber-salze auf dem Papier, und dann Zersetzung des Salzes mittels radioaktiven Iodid und Radiometrie der $Ag^{131}I$-Restes entwickelt. Die maximale Aktivität ist mit dem Logarithmus des Flecken-Gehaltes fur Fettsäuren Phosphaten, aber micht für Glykose-1-phosphat, proportional.

Résumé—On décrit une méthode que l'on propose d'appeler double décomposition radiochromatographique et qui consiste en l'analyse radiométrique d'acides gras saturés, de phosphates minéraux et de phosphate de glucosyl à partir des chromatogrammes sur papier: le sel d'argent insoluble est formé sur la bande de papier puis décomposé par l'iodure 131, on mesure alors la radioactivité de IAg déposé. L'activité totale des taches est une fonction linéaire de la composition de la tache. Le maximum (pic) d'activité de la tache est proportionnel au logarithme de la composition de la tache pour les acides gras et les phosphates mais non pour le phosphate de glucosyl.

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TITRIMETRIC DETERMINATION OF MANGANESE FOLLOWING NITRIC ACID OXIDATION IN THE PRESENCE OF PYROPHOSPHATE

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Summary—A new method for the determination of manganese is presented in which the element is oxidized to the tervalent state in strong phosphoric acid-pyrophosphate solution by means of nitric acid, and is then titrated with ferrous solution, using diphenylamine or diphenylamine sulphonate as an indicator. The method is applicable with little modification to a wide variety of materials, including steels, ores, and silicate minerals.

PRESENTLY available methods for the determination of manganese are in general fairly satisfactory. For small amounts, colorimetry or photometry based on the colour of the MnO_4^- ion in solution is the usual technique, and for large amounts the bismuthate method and the newer pyrophosphate method of Lingane and Karplus[2] are widely applied. The chief disadvantages of the bismuthate method are procedural; close attention to detail is necessary for good results, and because of the valence change a large amount of standard reducing substance must be used. In the method of Lingane and Karplus, the end-point is determined electrometrically, and there is no possibility of repeating the titration on the same solution.

The method proposed here is believed to be a decided improvement over any existing for the determination of moderate amounts of manganese. It utilizes the same valence change (II–III) as the Lingane and Karplus method, but in reverse, the manganese being quantitatively oxidized to the tervalent state, and then reduced with standard ferrous solution, diphenylamine or diphenylamine sulphonate being used as the indicator. In most instances no preliminary separations are necessary. The sample may be dissolved in any suitable acid and treated directly by the procedure to be described.

In strong phosphoric acid solution, Mn^{II} is oxidized to Mn^{III} by nitric or perchloric acids on heating, and by chromic acid in the cold, giving a coloured solution which resembles permanganate, but which is much less intense for the same amount of manganese. It is possible to make a photometric determination, utilizing the Mn^{III} colour, simply by adding to the Mn^{II} solution 3–4 times its volume of 85% phosphoric acid and an excess of dichromate. After allowing the solution to stand at room temperature for a few minutes to be sure that the oxidation is complete, the resulting colour is read photometrically. The excess chromate and the Cr^{III} formed in the reaction do not interfere, despite their intense colour, provided that the same amount of chromic acid is added to standards and unknowns. Perchloric, sulphuric, and nitric acids have no effect, but hydrochloric acid interferes. The spectrophotometry of Mn^{III} in phosphate solution has been studied by Tomula and Aho[4] and by Purdy and Hume,[3] who used bromate as the oxidant.

For the titrimetric determination, the oxidation of the manganese is best done with nitric acid, although perchloric or chromic acids may be used if the solution is heated sufficiently to decompose the chromate (either added or originating in the sample). In phosphoric acid solution chromate decomposes rapidly above 250°, and this temperature is easily attained on an electric hot plate. Photometry may also follow nitric acid oxidation of the manganese if convenient, but the titration is so simple and precise over such a wide range of manganese concentrations that it is preferred. So far as the writer has been able to determine, vanadium is the only interfering element, and it is quantitatively oxidized by nitric acid and reduced to V^{IV} by ferrous iron, so that it may be determined separately and a correction applied. It is possible that a potentiometric titration would permit the simultaneous determination of both elements.

EXPERIMENTAL

Reagents

Standard ferrous ammonium sulphate: 0.1 or 0.02*N* in 5% (v/v) sulphuric acid, preferably prepared fresh, with water which has been boiled to remove dissolved oxygen.

Diphenylamine: 0.2% aqueous solution of barium diphenylamine sulphonate, or a 1% solution of diphenylamine in concentrated sulphuric acid.

1 : 1 *nitric acid*: boiled to remove lower nitrogen oxides.

Procedure

To the Mn^{II} solution in a wide-mouth conical flask, which should preferably contain nitric acid as the only acid, and which should not have too large a volume, add 10 ml of 85% phosphoric acid plus an additional 15 ml for every 40 mg of MnO expected. Add 5 ml of nitric acid and evaporate on the hot plate, controlling the temperature so that evaporation takes place without boiling. Boiling phosphoric acid solutions is not recommended because of their extreme tendency to spatter. When the volume has been reduced to approximately that of the phosphoric acid used, add 5–6 g of sodium pyrophosphate for every 20 ml of phosphoric acid, and continue heating until the nitric acid is substantially all expelled, as indicated by the lack of condensation on the walls of the flask. Temperature is not a critical factor; the solution temperature will reach about 145° if the plate temperature is such that evaporation proceeds without boiling. Finally add 1 ml of 1 : 1 nitric acid (free from lower oxides of nitrogen) and continue heating for 10–15 minutes, during which time the nitric acid will reflux on the walls of the flask. Complete removal of nitric acid is undesirable.

Remove from the heat (before all the nitric acid is gone), cool until the flask can be handled, and add ¼ the volume of *cold* water. Mix and cool in running water. A larger addition of water at this stage may lead to slightly low results, particularly if the manganese concentration is near the maximum of approximately 2 mg of MnO per ml of phosphoric acid. The solution should not be allowed to cool completely before making the small addition of water, because it may become glassy and hard to dilute. When cold, dilute to about 20% in H_3PO_4, cool in running water, and titrate with standard ferrous solution, adding diphenylamine or diphenylamine sulphonate just before the end-point. It is best to delay the indicator addition until the pink colour of tervalent manganese is nearly discharged. The end point is extremely sharp, even with the 0.02*N* ferrous solution.

If a check on the titration is desired, add nitric acid and evaporate as before, and repeat the procedure.

Results obtained by the method on pure manganese solutions are given in Table I. For these titrations, a 0.1*N* ferrous solution in a 10-ml buret graduated to 0.02 ml was employed, and in each case 15 ml of 85% phosphoric acid was used. The ferrous solution was standardized against standard dichromate solution. The results indicate that with more than about 40 mg of MnO in this volume of phosphoric acid, it is difficult to oxidize the manganese completely. A safe limiting concentration is 2 mg of MnO per ml of phosphoric acid.

Many silicates may be decomposed by heating on the hot plate with phosphoric acid and sodium pyrophosphate, and this fact has been used to advantage in the determination of manganese in biotite, garnet, and other minerals. Chromite is decomposed only very slowly by the mixture, but dissolves reasonably quickly in perchloric acid.

The new method has been used successfully with little modification for the determination of manganese in tungsten steel, ferromanganese,[1] manganese minerals, and silicates. Some comparative results for various materials are given in Table II. In all cases, the ferrous solution was standardized against standard dichromate solution.

TABLE I. DETERMINATION OF MANGANESE IN PURE SOLUTIONS

MnO taken, *mg*	MnO found, *mg*
0.20	0.17
0.40	0.39
1.00	0.97
2.00	2.00
10.00	9.95
20.00	19.99
40.00	39.90
53.9	52.9

TABLE II. COMPARATIVE RESULTS

Sample	MnO present	MnO found
Garnet*	4.57 (gravimetric)	4.56
Garnet*	10.70 (gravimetric)	10.71
Garnet*	14.56 (gravimetric)	14.55
Garnet*	8.70 (gravimetric)	8.71
Phosphate mineral*	6.35 (gravimetric)	6.27 6.30
Biotite*	.89 (colorimetric)	.91
Bauxite*† (U. S. Bureau of Standards Sample No. 69)	.55	.54
Nickel-chromium steel‡ (U. S. Bureau of Standards Sample No. 32c)	.752§	.75§
Iron ore** (U. S. Bureau of Standards Sample No. 28a)	.435§	.45§
Manganese ore** (Bureau of Standards Sample No. 25b)	58.35§	58.54§

* Sample dissolved directly in phosphoric acid-sodium pyrophosphate on the hot plate.
† A large amount of material remained undissolved; result uncorrected for 0.03 V_2O_3.
‡ Sample dissolved in dilute nitric acid before adding phosphoric acid.
§ Reported as per cent Mn.
** Hydrochloric acid used to aid in solution of the sample.

DISCUSSION

Omission of the sodium pyrophosphate addition makes very little difference in the results, particularly if manganese is low. However, when the MnO concentration approaches the limit of approximately 2 mg per ml of phosphoric acid, complete oxidation is more certain in the presence of added pyrophosphate. When silicates are to be decomposed directly, the sodium pyrophosphate prevents the precipitation of silicic acid and greatly facilitates solution.

The addition of 1 ml of 1:1 nitric acid in the final stages of the procedure may be omitted when less than about 5 mg of MnO is in question, With larger amounts, oxidation is not quite complete unless this step is included. If the titrant is standardized against a similar material carried through the procedure, the extra addition could in many cases be omitted in routine analysis, with little effect on accuracy.

TABLE III. RESULTS FROM REPEATED TITRATIONS

Mineral	MnO found in first titration, *mg*	MnO found in second titration, *mg*	MnO present, *mg*
Tremolite	1.82	1.82	
Amphibole	13.83	13.94	13.88*
Rhodonite	44.96	45.18	45.15*

* Determined by the pyrophosphate method of Lingane and Karplus.[8]

With 4.0, 10.0, and 20.0 mg of MnO, 3.92, 9.97, and 18.68 mg were found when the final addition of nitric acid was omitted. In another experiment, in which the oxidation of the manganese was done with perchloric acid, with the same amounts of added manganese, 3.98, 9.91, and 19.4 mg were found. Care must be taken that the nitric acid is free from lower oxides, for they either reduce Mn^{III}, or are incompletely removed during the 10–15 minute heating period.

The silicate minerals which were dissolved directly in the phosphoric acid–sodium pyrophosphate mixture were ground to pass a 115-mesh screen. One to two hours heating, during which the temperature of the mixture approached 200°, sufficed for the garnets; biotite required only about 15 minutes. Iron ore and manganese ore required the preliminary use of hydrochloric acid. Hydrochloric acid should be removed (by repeated evaporation with nitric acid, or by fuming with perchloric acid) before adding the phosphoric acid. Steels should be dissolved, when possible, in dilute nitric acid before adding the phosphoric acid; however other solution procedures are sometimes necessary—for instance tungsten steels are best treated with mixed phosphoric and perchloric acids directly.

Chloride or perchlorate in the presence of nitrate can lead to erroneous results.

When large amounts of chromium are present, and particularly if perchloric acid is used as the oxidant, sulphate should be absent, for on occasion an insoluble precipitate separates (presumably $Cr_2(SO_4)_3$). Results are always low when this happens, probably because the precipitate carries down manganese.

The ferrous ammonium sulphate solution used in the titration may be standardized by any of the usual methods, but it is best to prepare a standard solution from manganese metal of known purity. Aliquot parts of this solution may then be run through the procedure at the same time as the unknowns.

When silicate minerals are dissolved directly in the phosphoric acid-sodium pyrophosphate mixture, there is some difficulty in determining whether or not attack is complete. In such cases, it is always advisable to evaporate the solution after titration, add more acid, and repeat the procedure. To illustrate this point the figures resulting from three determinations are given in Table III.

Acknowledgment—The author wishes to acknowledge the advice and assistance of S. S. Goldich in this work. Thanks are also due to E. B. Sandell and R. B. Ellestad for reading and commentary on the manuscript. The investigation was made possible by a grant from the Geological Society of America to the Rock Analysis Laboratory in support of research in methods of silicate analysis.

Zusammenfassung—Eien neue Methode zur Bestimmung von Mangan wird angegeben. Das Element wird in konzentrierter Phosphorsäure-pyrophosphat Lösung zu drei-wertigem Zustand mittels Saltpetersäure oxydiert, und wird dann mittels Eisen (II)-Lösung mit Diphenylamin-sulphonat als Indikator titriert. Die Methode ist durch geringe Modifikation auf eine grosse Mannigfaltigkeit von Materialien anwendbar, u.a. Stahlen, Erze und Silikat-Materialien.

Résumé—Une nouvelle méthode pour la détermination du manganèse est proposée. Dans cette méthode l'élément est oxydé au degré d'oxydation III dans une solution concontrée d'acide phosphorique et de pyrophosphate au moyen d'acide nitrique et est alors titré par une solution ferreuse utilisant de la diphénylamine ou de la diphénylamine sulfonée comme indicateur. La méthode peut être étendue avec peu de modification à une grande variété de substances, comprenant les aciers, les alliages et les silicates.

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THE SPECTROPHOTOMETRIC DETERMINATION OF CERIUM IN FLUORIDE SALTS

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Summary—Cerium^{III} in fluoride salt mixtures can be determined by measurement of its ultraviolet absorption peak at 253 mμ in 3*M* HCl. Over the range of 0 to 0.4 mg of Ce per millilitre, Beer's law is obeyed. The interfering ions, Fe^{III}, Cr^{VI}, and U^{VI}, are removed by extraction from a 7*M* HCl solution into a *cyclo*-hexane solution of tri-*n*-octylphosphine oxide. The method is rapid and precise and avoids difficulties which are encountered because of the instability of solutions which contain Ce^{IV}.

THE solubility of cerous fluoride in mixtures of fluoride salts such as $NaF–ZrF_4–UF_4$ (50–46–4 mole per cent) has been investigated by Ward, Strehlow, Grimes and Watson[11] who used $^{141}CeF_3$ as a tracer. In order to confirm their analytical data, chemical methods for the determination of cerium in fluoride salts were also investigated. The venerable oxalate precipitation method is not particularly applicable in this case, although, with sufficient care, reproducible and reliable numbers can be obtained. The titrimetric oxidation-reduction procedure is time-consuming and also requires considerable careful technique. For these reasons spectrophotometric methods were also considered. These are based either on the absorbance of a cerium^{IV} perhydroxide complex in basic solution[3,7,8,10] or the absorbance of cerium^{IV} in acidic media.[4,6] Neither of these absorbance measurements is entirely satisfactory because of turbidity problems encountered in basic solutions with cerium^{IV} and the instability of dilute cerium^{IV} solutions in acidic solutions.

Greenhaus, Feibush and Gordon[5] exploited the ultraviolet spectrum of cerium^{III} in sulphuric acid solution to determine cerium. Their method depends on the absorbance of cerium^{III} in 0.5*M* sulphuric acid at 253.6 mμ. Both zirconium and uranium interfere strongly with their method. In this report, suitable modifications are described by which the ultraviolet spectrophotometric technique can be successfully applied to the determination of Ce in $NaF–ZrF_4–UF_4$ and other fluoride salt mixtures.

REAGENTS AND APPARATUS

A concentrated stock solution of cerium^{III} was prepared by dissolving 2.342 g of spectrographically pure cerous oxide (Research Chemicals, Inc., Burbank, California) in 25 ml of water to which 15 ml of concentrated hydrochloric acid and 10 ml of concentrated sulphuric acid were added. The solution was heated to heavy fumes of sulphur trioxide prior to dilution to volume with water.

Tri-*n*-octylphosphine oxide (TOPO) (Distillation Products Industries): A 0.05*M* solution was prepared by dissolving 3 g of reagent in 200 ml of *cyclo*hexane.

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

RESULTS

Application to chloride solutions

In his investigation Greenhaus discovered that chloride ion could be present in high concentrations without effect upon the absorbance of cerium$^{\text{III}}$ in 0.5*M* sulphuric acid. Stewart and Kato[9] have also recently published the ultraviolet spectra of rare-earth chlorides in hydrochloric acid solution. As shown in Fig. 1, the ultraviolet spectra of cerium$^{\text{III}}$ in both sulphuric and hydrochloric acids are essentially identical. There are three absorption peaks, the maximum occurring at 253 mμ. At this wavelength, an absorbance index of 755 was reported by Stewart and Kato. The value found in this laboratory, 775, is in quite good agreement. Using Greenhaus' data the value for cerium$^{\text{III}}$ in sulphuric acid is 694. The adherence to Beer's law at 253 mμ is excellent; the straight line function of absorbance to concentration extends to 0.4 mg per ml at an absorbance of two. This relationship is shown in Fig. 2.

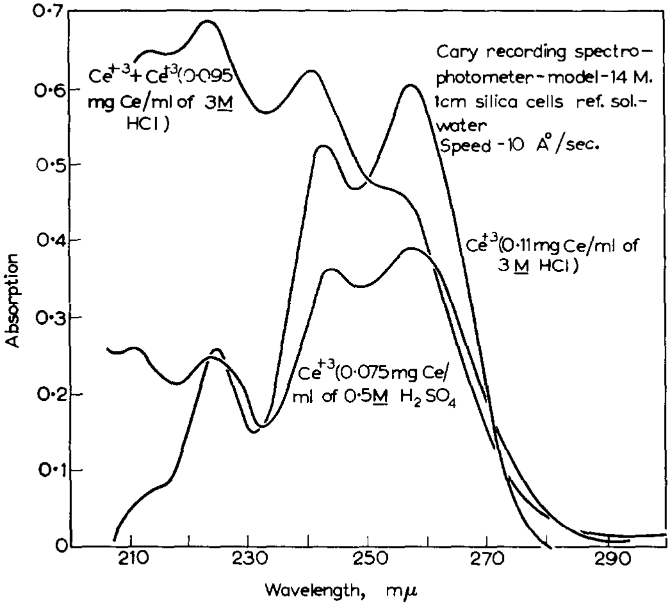

FIG. 1.

On the basis of these data, the ultraviolet absorbance technique is obviously applicable to chloride systems as well as sulphate solutions.

Effect of hydrochloric acid concentration

Tests were conducted to determine the optimum acid concentration of the cerium$^{\text{III}}$ solution. Aliquots of the stock solution were diluted with hydrochloric acid of various concentrations from 0.1 to seven molar. The absorbance spectra of these solutions were recorded immediately thereafter. In each case the reference solution was water.

The spectra are identical, indicating that no appreciable formation of any cerium$^{\text{III}}$ chloride complexes occur under these conditions in solutions less concentrated than 7*M* in HCl and that the cerium$^{\text{III}}$ ion is the light-absorbing species. Jorgensen[1] had reported some evidence for the formation of a cerium$^{\text{III}}$-chloride complex in solutions exceeding 5*M* HCl. This formation is not supported by the spectrophotometric data obtained in this investigation. In fact no change in absorbance spectra of cerium$^{\mathrm{III}}$ in 7*M* HCl was observed after 48 hours standing.

The absorbance of cerium$^{\mathrm{III}}$ is independent of acid concentration through 7*M* HCl. This independence from acid concentration is an important advantage in any spectrophotometric method because of the wide latitude that is available in establishing conditions for a working procedure.

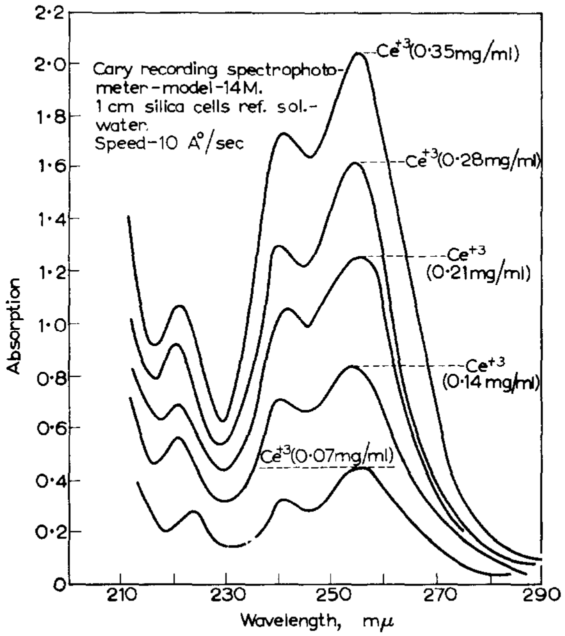

FIG. 2.

Effect of oxidation state of cerium

The presence of even trace amounts of cerium$^{\mathrm{IV}}$ in cerium$^{\mathrm{III}}$ could result in gross errors because the intensely yellow-coloured cerium$^{\mathrm{IV}}$ ion absorbs so strongly in the ultraviolet that it completely obliterates the absorbance peaks of cerium$^{\mathrm{III}}$ (see Fig. 3). Greenhaus found that in 0.5*M* H_2SO_4, as little as 1 μg per ml of cerium$^{\mathrm{IV}}$ caused an error of 3% in the determination of the cerium$^{\mathrm{III}}$ concentration.

In hydrochloric acid, however, the interference of cerium$^{\mathrm{IV}}$ is eliminated because of the oxidation-reduction reaction

$$Ce^{4+} + HCl \rightarrow Ce^{3+} + \tfrac{1}{2}Cl_2 + H^+. \qquad (1)$$

Hydrochloric acid in high concentrations drives this reaction to the right, as written, so that the concentration of cerium$^{\mathrm{IV}}$ in strong acid at equilibrium is indeed quite small. The reaction is quite dependent, however, on the concentration of HCl. This dependence is shown strikingly in Fig. 3. In 1*M* HCl, little reduction of cerium$^{\mathrm{IV}}$ occurs; the solution absorbs ultraviolet light so strongly that the cerium$^{\mathrm{III}}$ absorbance peak at 253 mμ is unobservable. The influence of HCl begins to become evident at 3*M* HCl, some cerium$^{\mathrm{III}}$ obviously being present. At 7*M* HCl the reduction is quantitative; the absorbance at 253 mμ is equivalent to that of pure cerium$^{\text{III}}$, which had been treated with hydroxylamine hydrochloride to insure complete reduction of any cerium$^{\text{IV}}$ to the tervalent state.

From the standpoint of effect of the oxidation state, strong hydrochloric acid media, therefore, have obvious advantages over sulphuric acid with respect to the interference of cerium$^{\text{IV}}$.

Effect of diverse elements

Although the main interference, cerium$^{\text{IV}}$, is effectively eliminated through the use of strong hydrochloric acid media, knowledge of the effect of zirconium, uranium, beryllium and thorium on the ultraviolet spectrophotometric determination of cerium was required before the method could be applied to molten salt reactor fuels.

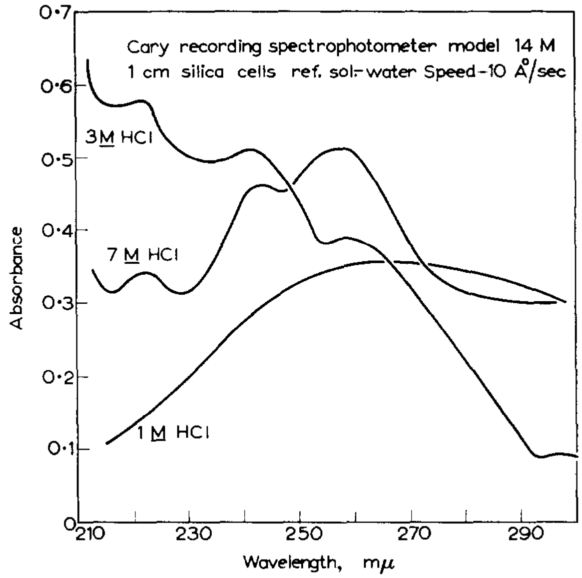

FIG. 3. Ce, 1 mg per ml.

Elements which are known to interfere with the ultraviolet spectrophotometric determination of cerium$^{\text{III}}$ are limited to those that have appreciable absorbance in the ultraviolet region.[2] Foremost of these are iron$^{\text{III}}$, titanium$^{\text{IV}}$, copper$^{\text{II}}$, uranium$^{\text{VI}}$, molybdenum$^{\text{VI}}$, zirconium$^{\text{IV}}$, hafnium$^{\text{IV}}$, and thorium$^{\text{IV}}$. Of the common anions, only nitrate presents much difficulty. Large amounts of either phosphate or perchlorate can be tolerated as long as no precipitation occurs.

In the application of this method to the analysis of fluoride salts and mixtures thereof, some of these interferences are eliminated by the procedure used for dissolving the fluoride salts. The fluoride salt is heated to strong fumes of sulphur trioxide, which removes fluoride and nitrate, if present, and converts the fluoride salt to the sulphate salt.

Copper and molybdenum do not commonly occur in these mixtures, and, if so, only in small concentration. They can be separated more or less completely from cerium by precipitation of the cerium with ammonia. In this precipitation zirconium, uranium, thorium and beryllium, which are major components of these solutions, also precipitate as insoluble hydrous oxides. Although this step ensures the completeness of the precipitation of cerium, copious amounts of elements that are known to interfere with this method must thus be removed in some manner.

White and Ross[12] in their studies of the extraction characteristics of tri-*n*-octylphosphine oxide (TOPO) have shown that this reagent is extremely effective in the extraction of zirconium, thorium, uranium, titanium, and iron from strong hydrochloric acid solution. They reported that cerium$^{\mathrm{III}}$ did not extract under these acidic conditions. Since 7*M* HCl is the preferred medium for reducing any cerium$^{\mathrm{IV}}$ that might be present, the separation of these metals from cerium by extraction with TOPO was tried.

Two weight ratios of interference to cerium were tested, the first, approximately 4 : 1 and the second, 10 : 1. The latter ratio is about the greatest difference in concentration that would ever likely be encountered in these fluoride salt mixtures. About 3 mg of cerium was used in each test and the 7*M* HCl solution was extracted with 10 ml of 0.2*M* tri-*n*-octylphosphine oxide in *cyclo*hexane.

Uranium, molybdenum, thorium, zirconium, beryllium, iron, and titanium did not interfere at either concentration level tested. This attests the efficiency of the extraction, since as little as 0.5 μg Fe per ml or 4 μg U per ml will increase the cerium result by 3%. As previously mentioned, copper and molybdenum are at least partially removed by the basic hydroxide precipitation. About 1 μg of either of these elements per ml will also produce a three per cent error in the cerium value.

TABLE I. EFFECT OF DIVERSE ELEMENTS ON THE METHOD AFTER EXTRACTION WITH TOPO

Element	Weight ratio $\left(\frac{\text{element}}{\text{cerium}}\right)$	Error, %
Fe^{+3}	10	<1
Ti^{+4}	10	<1
Cu^{+2}	10	<1
UO_2^{+2}	10	<1
Mo^{+6}	10	<1
Zr^{+4}	10	<1
Cr^{+6}	4	+4
Cr^{+6}	10	+25

The only interference not eliminated by this extraction is chromium. Although hexavalent chromium is extracted by TOPO from hydrochloric acid solutions, in 7*M* HCl, hexavalent chromium is reduced to trivalent chromium, at which oxidation state chromium is not extracted. When present in a concentration three times that of cerium, chromium produces a 4% error. At the 10 : 1 level, the error is about 25%. Fortunately, chromium occurs in these fluoride salts as a corrosion product and rarely exceeds 1000 ppm. Chromium, therefore does not present too difficult a problem in this particular application. The effects of the diverse elements are summarized in Table 1.

Precision of the method

The precision of the method was determined at three concentration levels of cerium, approximately 0.4 mg, 1, and 3 mg Ce. In all tests the zirconium and uranium concentrations were equivalent to those normally encountered, that is 10 to 30 times that of cerium. The overall coefficient of variation is 1%. There is no indication of a bias on the basis of these data.

TABLE II. PRECISION AND ACCURACY OF THE METHOD

Cerium, *mg*, present	0.336	1.13	3.00
Number of determinations, N	4	4	4
Average, $\bar{x}$	0.336	1.14	3.01
Coefficient of variation, %	0.92	1.0	1.4

Comparison with radio-tracer method

Typical results for cerium as analyzed by the ultraviolet spectrophotometric method and the radio-tracer technique[11] are illustrated in Table III. The results are in excellent agreement over a wide range of cerium concentrations. The average difference is less than 2%.

TABLE III. TYPICAL RESULTS FOR THE COMPARISON OF THE SPECTROPHOTOMETRIC METHOD TO THE RADIO-TRACER DETERMINATION OF CERIUM

Cerium, %		Difference A - B
Spectrophotometric A	Radio-tracer B	
0.40	0.37	+0.03
.64	.59	+0.05
.88	.83	+0.05
1.15	1.14	+0.01
1.91	1.97	−0.06
2.27	2.35	−0.08
2.41	2.34	+0.07
3.88	3.78	+0.10
7.62	7.53	+0.09
8.00	8.16	−0.16
8.67	8.72	−0.05
8.90	8.88	+0.02

Average	0.064
Coefficient of variation, %	4.08
Overall agreement	2%

RECOMMENDED PROCEDURE

Weigh a 2- to 5-g sample of fluoride salt to the nearest 10 mg and transfer to a platinum dish. Add about 1 g of boric acid and mix the solids. To the ultimate mixture add 5 ml of concentrated nitric acid, 20 ml of concentrated hydrochloric acid and 25 ml of concentrated sulphuric acid. Heat to strong fumes of sulphur trioxide and then dilute to 500 ml with water.

Transfer an aliquot, no larger than 10 ml, which contains preferably 0.5 to 5.0 mg of cerium, to a 15-ml centrifuge tube. Add concentrated ammonium hydroxide dropwise until the cerium is precipitated; then add about 2 ml excess and cool. Centrifuge the samples for two minutes. Decant the supernatant liquid and dissolve the precipitate in 10 ml of 7*M* hydrochloric acid. Transfer the solution to a 25-ml volumetric flask; then dilute to volume with 7*M* HCl. Transfer the solution to a 60-ml separatory funnel and add 5 ml of 0.05*M* TOPO in *cyclo*hexane; then shake the sample for two minutes. Allow the phases to separate and collect the aqueous phase in a 25-ml volumetric flask. Measure the absorbance at 253 mμ against water.

Zusammenfassung—Man kann Cer(III) in Fluorid-Salz-Mischungen durch Messung bei 253 mμ in 3*M* Salzsäure bestimmen. Im Bereich 0 bis 0,4 Milligrammen von Cer pro millilitre folgt die Lösung das Beer'schen Gesetz. Die störende Ionen, Fe(III), Cr(VI), und U(VI) werden durch Extraktion aus einer 7*M* Salzsäure Lösung in eine Cyclohexan-Lösung von Tri-*n*-octylphosphinoxyd entfernt. Die Methode ist rasch und präzis.

Résumé—On peut utiliser l'absorption maximale à 253 mμ en 3*M* HCl pour le dosage de Ce(III) en présence de fluorure. La loi de Beer est suivie quand la concentration de Ce est de 0 à 0,4 mg/ml. Les ions Fe(III), Cr(VI) et U(VI), qui gênent, sont extraits à l'aide de l'oxyde de tri-*n*-octylphosphine en milieu cyclohexane. Cette méthode, qui est rapide et précise, évite les difficultés produites par l'instabilité de solutions de Ce(IV).

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SHORT COMMUNICATIONS

Ferrous iron-sulphuric acid reagent for the determination of pure œstrogens*

(*Received* 26 *August* 1958)

THE work of Wieland *et al.*[8] in 1929 established the fact that œstrone produces a green-gold colour with a blue-green fluorescence when treated with concentrated sulphuric acid. In 1930, Marrian,[7] described an orange colour with green fluorescence when œstriol was heated with concentrated sulphuric acid. In an investigation of these effects, Kober[6] in 1931 described a procedure for œstrogenic steroids which procedure now bears his name and covers a multitude of modifications and adaptations of the original method. In 1952, Brown[2] in a comprehensive study of the Kober reaction, found that reducing agents tended to induce a more intense colour reaction when used in the Kober test. Ferrous sulphate was reported as exerting the most pronounced effect.

Although the mechanism of the Kober reaction remains obscure and many reported conditions involving the colour reaction are seemingly contradictory, several salient facts reported in the recent literature concerning this process are of interest. Brown,[2] in his investigation of the Kober reaction, reported that the presence of a reducing agent in the first stage of the two stage process is necessary for full colour development. He also points out that the oxidizing agents such as ferric sulphate and hydrogen peroxide accelerate the red colour formation in the second stage but cause subsequent fading. Brown concludes that "... the reducing agents and their oxidized forms may poise" the reaction conditions so that the red colour can form by oxidation without simultaneous destruction by further oxidation.

The work reported by Haenni[5] would seem to lend credence to such a view even though reaction conditions were far different. Using ferric iron and phenol in sulphuric acid a stable and sensitive reaction resulted. The inference is again that a controlled oxidation took place.

The Kober colour can be formed through the mediation of other reactions. In a *p*-toluenesulphonic acid spot test[3] reported recently by the present authors, œstrogens when fused with the acid salt developed a red or orange colour with intense fluorescence. This coloured material when dissolved in concentrated phosphoric acid showed an absorption peak at 515 mμ (Coleman Universal). A similar reaction with methylenedisalicylic acid was reported by Feigl.[4] Further, one of the present authors has observed that œstrogen exposed to an atmosphere of sulphur trioxide (made by heating concentrated sulphuric acid in a closed vessel) develops a red colour. On the other hand, Axelrod[1] used fuming sulphuric acid with various steroids but did not report a colour absorbing in the vicinity of 510 mμ with œstrogens.

In all the aforementioned papers the procedure was carried out in two stages. In this study a ferrous ammonium sulphate-sulphuric acid reagent is used in a one-step procedure to estimate quantitatively œstradiol, œstrone and œstriol.

APPARATUS AND REAGENTS

Chemicals were of reagent grade and all solutions were prepared in distilled water. The sulphuric acid used was the nine-pound per bottle variety.

Ferrous ammonium sulphate, hexahydrate.

Œstrone: purified crystals, m.p. 252–253°.

Œstradiol (œstradiol-17 β) purified crystals, m.p. 173–174°.

Œstriol, purified crystals, m.p. 272–273.5°. Œstrogens supplied by courtesy of Schering Corp.

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* Supported by Research Grant A–121–C from the Division of Research Grants and Fellowships of the National Institutes of Health.

Sulphuric acid, 52% (by volume).

Sulphuric acid, 70% (by volume).

Œstradiol-œstrone acid reagent: 290 mg of ferrous ammonium sulphate are mixed with 52% sulphuric acid (ferrous-acid reagent) to make 100 ml total volume. It remains stable for approximately three days if protected from air.

Œstriol acid reagent: 290 mg of ferrous ammonium sulphate are dissolved in 7.5 ml of distilled water and 70% sulphuric acid is added to make 100 ml total solution of 65% sulphuric acid at room temperature.

COLOUR DEVELOPMENT

Œstrone:

Measured amounts of œstrone solution are pipetted into Coleman Spectrophotometer 19 × 150 mm round cuvettes and the solvent is evaporated off in a water bath. Eight ml of 52% ferrous-acid reagent are delivered into each cuvette from a burette. The solutions are heated for 50 minutes in a boiling water bath. At the end of this period the tubes are cooled to room temperature and read at 505 mμ.

Œstradiol:

In the same manner, measured amounts of œstradiol solution are heated with 52% ferrous-acid reagent in a boiling water bath for 30 minutes. The developed colours are read at room temperature at 505 mμ.

Œstriol

Measured amounts of œstriol are heated with 65% ferrous-acid reagent for 50 minutes in a boiling water bath. After cooling, the developed colours are read at 500 mμ.

RESULTS OF COLOUR REACTIONS WITH PURE ŒSTROGENS

As shown in Table I 4.3 μg of œstrone in 8 ml of solution (0.54 μg per ml) can be readily detected by this technique. The mean value at each concentration level is shown with the average deviation. Absorbance values for œstradiol and œstriol were obtained for similar numbers and weights of samples as described for œstrone. Weight of sample, mean absorbance and average deviation are given in Table I. Range of reproducibility values for œstrone was found to be 3–9%, usually 3–5%; for œstradiol, 5–8%; for œstriol, 1–5%.

NOTES

1. Œstrone shows maximum absorbance in a range between 50–60% sulphuric acid. Œstradiol has a somewhat narrower range, namely 50–55%, while œstriol shows a peak absorbance in 65% sulphuric acid.
2. The time required to develop maximum colour for œstrone at 100° is 50 minutes. Œstradiol and œstriol require 30 minutes of heating, the latter showing no change in absorbance after 50 minutes.
3. A plateau of colour development is obtained with 20–56 mg of ferrous salt per 8 ml of volume.
4. Using a Beckman Du Spectrophotometer the absorption maxima for œstrone and œstradiol were found to be 512 mμ and that for œstriol 505 mμ. The $E^{1\%}_{1\,\text{cm}}$ for œstrone, œstradiol and œstriol were 1350, 1362 and 1289 respectively.
5. The œstrone colour reaction obeys the Beer-Lambert law up to about 17.5 μg after which there is a perceptible curvature. This is due to the fact that this œstrogen, as well as œstradiol and œstriol, develops considerable fluorescence in sulphuric acid solution. At higher concentrations, under these conditions, the Beer-Lambert law does not hold.

The calibration curve for œstradiol is linear for about the same distance and shows the same curvature at concentrations greater than 20 μg. Œstriol presents a calibration curve similar to that of œstrone and œstradiol, remaining, however, linear to about 33 μg before deviations are noticed.

6. Colour formation tends to develop into the 520 mμ region in the case of sulphuric acid alone, but the curve is broad, presents no sharp absorption peak, and indicates less sensitivity than in the case of the ferrous-acid reagent. Using the latter reagent the absorption peak is sensitive, and well defined.

Table I. Colour reaction of œstrogens using the ferrous-sulphuric acid reagent

	Micrograms of œstrone (52% sulphuric acid)				
	4.3	8.6	17.2	25.8	34.4
Absorbance	0.085 0.087 0.070 0.068 0.074	0.148 0.150 0.160 0.149 0.157 0.160 0.160 0.152 0.145 0.160 0.155 0.150 0.160	0.282 0.326 0.292 0.298 0.286 0.325 0.313 0.320 0.287 0.312	0.445 0.378 0.461 0.425 0.460 0.447 0.460 0.430	0.572 0.570 0.540 0.595
Mean absorbance	0.077	0.155	0.304	0.438	0.569
Average deviation	0.007	0.005	0.016	0.021	0.015

	Micrograms of œstradiol (52% sulphuric acid)				
	4.6	9.2	18.4	27.6	36.8
Mean absorbance	0.081	0.166	0.317	0.482	0.558
Average deviation	0.007	0.012	0.017	0.025	0.038

	Micrograms of œstriol (65% sulphuric acid)				
	4.1	8.2	16.4	24.6	32.8
Mean absorbance	0.062	0.124	0.272	0.416	0.542
Average deviation	0.003	0.004	0.010	0.004	0.010

7. Ferric iron hastens colour production but promotes fading. It also lessens absorbance for œstrone and œstradiol despite the presence of ferrous iron. It appears to have no depressing effect on œstriol.

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Determination of zirconium in high temperature alloys

(*Received* 24 *November* 1958)

It is known that small amounts of boron and zirconium play an important role in improving the physical properties of nickel-base high-temperature alloys. There is need of a sensitive and selective method of determining the zirconium content in the high temperature alloys. A highly selective colour reaction for zirconium (and hafnium) with Xylenol Orange has been reported.[1] This short note describes a simple procedure of determining small amounts of zirconium in alloys, using Xylenol Orange.

Procedure: Dissolve by gentle heating one gram of alloy sample with 30 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid. Add 30 ml of 1:1 sulphuric acid, heat and fume a few minutes. Cool and dilute with water to approximately 100 ml. Separate nickel, cobalt, and other metals by mercury cathode (Dyna Cath) at 15 amperes until giving negative or very faint thiocyanate test for molybdenum. Precipitate zirconium and titanium by adding 10*N* sodium hydroxide and digest for 15 minutes on a hot-plate. Filter through a No. 42 Whatman filter paper and

TABLE I. DETERMINATION OF ZIRCONIUM IN HIGH TEMPERATURE ALLOY

Sample	Zirconium, %	
	Present†	Found
M-252* No. 2	0.035 0.039	0.038
M-252 No. 6	0.122 0.130	0.129

* M-252 contains approximately 20% Cr, 10% Co, 10% Mo, 3% Ti, 1% Al, Ni base, and traces of B and Zr.

† Determined by the gravimetric phosphate method after the mercury cathode and cupferron separations

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wash three times with hot water. Dissolve the precipitates on the filter paper with hot 0.8*N* perchloric acid into a 250-ml volumetric flask. Cool and make to volume with 0.8*N* perchloric acid. Take a suitable aliquot for the colour development with Xylenol Orange as described elsewhere.[1]

The results shown in Table I are excellent. It is believed that this procedure would be suitable for determining small amounts of zirconium in other types of alloys.

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Studies on organic reagents for inorganic analysis—V
m-Nitrophenylfluorone for the spectrophotometric determination of zirconium

(*Received* 18 *July* 1958)

FOR the determination of zirconium, phenylfluorone (abbreviation of 2:3:7-trihydroxy-9-phenylfluorone) method was recommended previously by the author and K. Kimura.[1] The reactions between phenylfluorone and several metals were also studied.[2,3] The method, which is about forty times more sensitive than the Alizarin Red S method,[4] is the most sensitive method hitherto reported for the colorimetric determination of zirconium, but the absorbance of the chelate decreases with increasing acidity in the solution. On the other hand, several derivatives of phenylfluorone were synthesized by the author, and the effect of the substituent on the utility of the derivatives as a spectrophotometric reagent was studied.[5,6] The results suggested that *m*-nitrophenylfluorone [abbreviation of 2:3:7-trihydroxy-9-(3′-nitrophenyl)fluorone] was one of the most excellent reagents for the pruopse in view of the sensitivity, stability, and other properties. In this paper, a detailed procedure for the spectrophotometric determination of zirconium using this reagent is described.

EXPERIMENTAL AND RESULTS

Apparatus and reagents used

The absorbance measurements were made with a UVISPEK spectrophotometer using 10-mm glass cell. The reference cell contained distilled water for all the measurements, except for the measurement of the absorption spectrum of the chelate, in which the blank solution was used as a reference solution.

Ethanolic solution of m-*nitrophenylfluorone*: *m*-Nitrophenylfluorone, was synthesized from hydroxyhydroquinone triacetate and *m*-nitrobenzaldehyde according to the method reported previously,[2,3] and 0.120 g of this reagent was dissolved in 150 ml of ethanol and 1 ml of 5*N* hydrochloric acid by warming. After being cooled, the solution was diluted to 200 ml with ethanol.

Zirconyl chloride stock solution: analytical grade zirconyl chloride octahydrate dissolved in 1*N* hydrochloric acid, and standardized gravimetrically using distilled ammonium hydroxide. This solution should contain 2.07 mg of zirconium per ml. A fresh working solution was prepared from the stock solution by dilution with dilute hydrochloric acid, for each experiment.

Cyclohexanol: Reagent grade *cyclo*hexanol without any purification.

Ethanol: Reagent grade 100% ethyl alcohol.

Spectral absorbance data for the reagent blank and 20.7 μg of zirconium (following the standard procedure mentioned later) are given in Fig. 1. The absorption maximum of the dye and the chelate was found at 475 mμ and 550 mμ, respectively. The optimum wavelength was taken as 550 mμ because at this point the absorption given by the blank solution is small and that by zirconium *m*-nitrophenylfluoronate is maximum.

wash three times with hot water. Dissolve the precipitates on the filter paper with hot 0.8N perchloric acid into a 250-ml volumetric flask. Cool and make to volume with 0.8N perchloric acid. Take a suitable aliquot for the colour development with Xylenol Orange as described elsewhere.[1]

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Apparatus and reagents used

The absorbance measurements were made with a UVISPEK spectrophotometer using 10-mm glass cell. The reference cell contained distilled water for all the measurements, except for the measurement of the absorption spectrum of the chelate, in which the blank solution was used as a reference solution.

Ethanolic solution of m-*nitrophenylfluorone*: *m*-Nitrophenylfluorone, was synthesized from hydroxyhydroquinone triacetate and *m*-nitrobenzaldehyde according to the method reported previously,[2,3] and 0.120 g of this reagent was dissolved in 150 ml of ethanol and 1 ml of 5N hydrochloric acid by warming. After being cooled, the solution was diluted to 200 ml with ethanol.

Zirconyl chloride stock solution: analytical grade zirconyl chloride octahydrate dissolved in 1N hydrochloric acid, and standardized gravimetrically using distilled ammonium hydroxide. This solution should contain 2.07 mg of zirconium per ml. A fresh working solution was prepared from the stock solution by dilution with dilute hydrochloric acid, for each experiment.

Cyclohexanol: Reagent grade *cyclo*hexanol without any purification.

Ethanol: Reagent grade 100% ethyl alcohol.

Spectral absorbance data for the reagent blank and 20.7 μg of zirconium (following the standard procedure mentioned later) are given in Fig. 1. The absorption maximum of the dye and the chelate was found at 475 mμ and 550 mμ, respectively. The optimum wavelength was taken as 550 mμ because at this point the absorption given by the blank solution is small and that by zirconium *m*-nitrophenylfluoronate is maximum.

Effect of cyclohexanol and ethanol concentration

A precipitate of zirconium *m*-nitrophenylfluoronate forms after a time from solution containing no *cyclo*hexanol and less than 5 ml of ethanol. The coloured solution becomes stable with increasing amount of *cyclo*hexanol added, but a *cyclo*hexanol layer separates from the ethanolic water layer above a certain proportion of *cyclo*hexanol to the amount of ethanol added. The solution shows no difference in the position of the absorption maximum when the amount of *cyclo*hexanol or ethanol added is altered, although there is a slight difference in the detailed shape of the absorption curve.

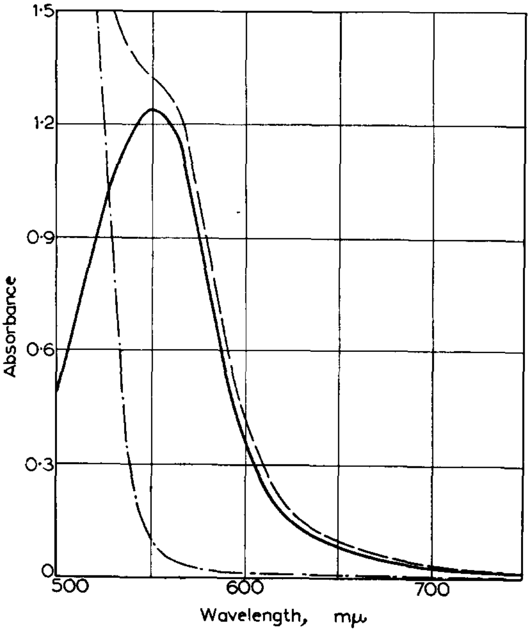

FIG. 1. Absorption curve. — · — blank solution (ref. solution, water);
- - - - Zirconium-dye complex (ref. solution, blank solution);
—— Zirconium-dye complex (ref. solution, blank solution).

From these results, 2.5 ml of *cyclo*hexanol, 5 ml of ethanol, and 5 ml of ethanolic solution of *m*-nitrophenylfluorone were optimum. In this condition, the solution gives no visible precipitate of *m*-nitrophenylfluoronate with a zirconium concentration below 3 μg per 25 ml if allowed to stand for a day or more.

Effect of acidity

In the acidity range higher than 1.5*N* hydrochloric acid concentration, the absorbances increase slowly with increasing digestion time. The absorbance is almost independent of hydrochloric acid concentration in the region below 0.1*N* whereas no plateau range is found above 0.05*N* acid concentration in the case of phenylfluoronate.

Effect of digestion time

In a solution containing more than 4 μg zirconium, a precipitate of zirconium *m*-nitrophenylfluoronate is obtained when the solution is allowed to stand for a day, but the stable suspension may be regenerated on short shaking by hand. The absorbance is nearly constant for forty minutes after the preparation.

Standard procedure

The following is recommended as an optimum procedure.

Transfer the sample solution (less than 10 ml) to a 25-ml volumetric flask. If the sample is known to contain more than 20 to 25 μg zirconium, an aliquot portion of the sample solution containing the desired amount of zirconium in a final volume is pipetted into a 25-ml volumetric flask. Additional acid will then be required to bring the acidity up to 0.10*N* hydrochloric acid used in the determination of zirconium with *m*-nitrophenylfluorone. Adjust the volume to about 10 to 12 ml with distilled water. Add 5 ml of ethanol, 2.5 ml of cyclohexanol, and 5 ml of ethanolic solution containing 3 mg of *m*-nitrophenylfluorone, in this order. Make the solution to the mark with distilled water, mix with shaking by hand, allow to stand for an hour, and obtain the absorbance of the solution in the spectrophotometer at 550 mμ using 10-mm glass cells and distilled water as a control solution. Determine the amount of zirconium by reference to the standard working curve prepared previously.

TABLE I.—INTERFERING IONS

Ion	Amount added, *ppm*	Error, %	Permissible amount, *ppm*
Fe^{II}	2.0	2	3
Fe^{III}	2.0	10	0.6
Ti^{IV}	0.2	40	0.01
Ge^{IV}	0.4	20	0.06
Sn^{IV}	0.4	10	0.1
As^{III}	10	2	15
As^{V}	10	10	3
Sb^{III}	2	10	0.6
Sb^{V}	2	10	0.6
F^-	2	25	0.2
$C_2O_4^{2-}$	5	20	0.7
HPO_4^{2-}	5	20	0.7

Working curve

A straightline relationship exists between absorbance and amount of zirconium up to 0.6 ppm. Solutions containing from 0.6 to 10 ppm deviate slightly from Beer's law but their absorbances are reproducible. The region from 0 to 0.10 ppm of zirconium was examined in detail for any deviation from the straight-line relationship, but none was found.

Effect of diverse ions

The effect of various ions was studied using 0.3 ppm of zirconium. The standard procedure was employed, except that the desired amount of the other ion was added to a volumetric flask before the addition of zirconium solution. The concentrations of zirconium and other ion are expressed on the basis of the final volume 25 ml. The change in absorbance was then measured at 550 mμ. Errors of less than 3% of the zirconium present were considered to be negligible. A negligible error was obtained with the following approximate maxima:

2000 ppm of:	sodium, potassium, ammonium, and magnesium ion.
1000 ppm of:	calcium, barium, strontium, and mercuric ion.
500 ppm of:	lanthanum, neodymium, cerrous, cadmium, zinc ion.
100 ppm of:	aluminium, and thorium ion.

Chloride, bromide, nitrate (2000 ppm) and sulphate (1000 ppm) ions do not interfere with the reaction.

Some elements interfere by increasing the colour intensity. Some elements quench the colour given by zirconium *m*-nitrophenylfluoronate. Table I lists the interfering ions and their effect.

Serious interference is given by the following ions: titanium, germanium, tin, iron, antimony, oxalate, phosphate and fluoride tested.

DISCUSSION

The colour change resulting from the reaction of *m*-nitrophenylfluorone with zirconium closely resembles that with phenylfluorone, namely the shift of the absorption maximum caused by chelate formation is 75 mμ in *m*-nitrophenylfluorone, and 72 mμ in phenylfluorone,[2] whereas the differences of the absorption maximum between the phenylfluorone or its zirconium chelate and *m*-nitrophenylfluorone or its zirconium chelate are 7 and 10 mμ, respectively. The trend in the effect of the acidity of the solution on the absorbance is, however, considerably different. In the *m*-nitrophenylfluorone method, recommended here, the constancy of the absorbance is obtained at the region of the acidity below 0.10*N* hydrochloric acid concentration, whereas there is no such constancy in phenylfluorone method. This may be caused by the effect of *m*-nitro group, in attracting the electron of the -OH group at the 3 position and increasing the electronegativity of the oxygen atom. Furthermore, the absorbance of *m*-nitrophenylfluoronate is greater than that of the corresponding phenylfluoronate. The sensitivity of this method, given by the slope of the working curve, is nearly fifty times that for the Alizarin Red S method,[4] about five times that for the quercetin method,[7] and about 1.2 times that for the phenylfluorone method.[1] In the region from zero to 0.15 ppm of zirconium the solution may be kept without any visible precipitation for three days or more. The method is therefore excellent for the determination of micro amounts of zirconium.

Acknowledgement—The author is indebted to Dr. Kenjiro Kimura, Professor Emeritus and Dr. Nobufusa Saito, Professor in this laboratory, for their encouragement to carry out this study. This work was supported partly by a grant from the Ministry of Education.

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The use of the pool cathode in polarography

(*Received* 1 *September* 1958)

INTRODUCTION

POLAROGRAPHY using a mercury pool as cathode instead of the conventional dropping mercury electrode (DME) has been described previously,[1-3] and increased sensitivity over the DME has been claimed for conventional polarographs. The main difficulty in the design of such cells is ensuring a closely reproducible pool size, as the cell current is directly proportional to the pool area. This is overcome in the cell used in the work described below by using a glass cup as the pool container, and filling the cup to overflowing every time a pool is used. This cell was designed by Mrs. B. Lamb of Tinsley Industrial Instruments Limited, and supplied by them. The cell is of the conventional H type, using a saturated calomel anode, with connection to the cathode compartment via an agar plug. The cell is shown in Fig. 1.

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The colour change resulting from the reaction of *m*-nitrophenylfluorone with zirconium closely resembles that with phenylfluorone, namely the shift of the absorption maximum caused by chelate formation is 75 mμ in *m*-nitrophenylfluorone, and 72 mμ in phenylfluorone,[2] whereas the differences of the absorption maximum between the phenylfluorone or its zirconium chelate and *m*-nitrophenylfluorone or its zirconium chelate are 7 and 10 mμ, respectively. The trend in the effect of the acidity of the solution on the absorbance is, however, considerably different. In the *m*-nitrophenylfluorone method, recommended here, the constancy of the absorbance is obtained at the region of the acidity below 0.10*N* hydrochloric acid concentration, whereas there is no such constancy in phenylfluorone method. This may be caused by the effect of *m*-nitro group, in attracting the electron of the -OH group at the 3 position and increasing the electronegativity of the oxygen atom. Furthermore, the absorbance of *m*-nitrophenylfluoronate is greater than that of the corresponding phenylfluoronate. The sensitivity of this method, given by the slope of the working curve, is nearly fifty times that for the Alizarin Red S method,[4] about five times that for the quercetin method,[7] and about 1.2 times that for the phenylfluorone method.[1] In the region from zero to 0.15 ppm of zirconium the solution may be kept without any visible precipitation for three days or more. The method is therefore excellent for the determination of micro amounts of zirconium.

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Polarography using a mercury pool as cathode instead of the conventional dropping mercury electrode (DME) has been described previously,[1-3] and increased sensitivity over the DME has been claimed for conventional polarographs. The main difficulty in the design of such cells is ensuring a closely reproducible pool size, as the cell current is directly proportional to the pool area. This is overcome in the cell used in the work described below by using a glass cup as the pool container, and filling the cup to overflowing every time a pool is used. This cell was designed by Mrs. B. Lamb of Tinsley Industrial Instruments Limited, and supplied by them. The cell is of the conventional H type, using a saturated calomel anode, with connection to the cathode compartment via an agar plug. The cell is shown in Fig. 1.

CONVENTIONAL POLAROGRAPHY

When this cell is used with a conventional polarograph, a peaked polargram similar to those normally obtained with the cathode ray polarograph is obtained, in which peak height is proportional to concentration; sensitivity is increased by a factor of about 20. This is in agreement with the findings of earlier workers.[1–3]

There are, however, severe drawbacks to the use of the pool cathode cell with this type of instrument, namely:

1. Each cell must be calibrated independently, as cell current varies with pool area. This is much more inconvenient than calibrating a single capillary which can then be used with any number of cells. In practice, it is easier to use the same cell for all determinations, which takes much longer than the usual procedure.

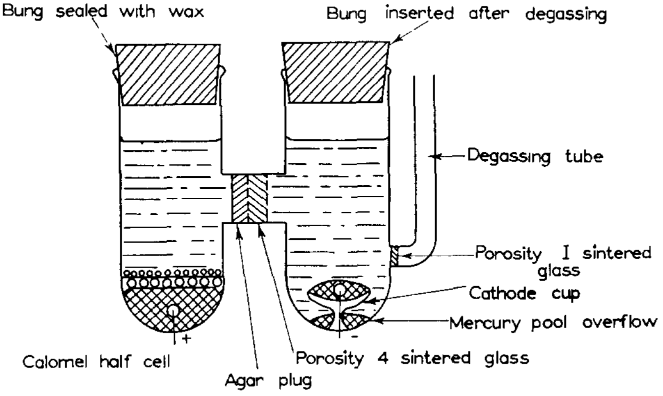

FIG. 1

2. Owing to the increased sensitivity of the electrode, the problem of residual oxygen becomes much more acute, as even after prolonged passage of hydrogen or nitrogen there is always an appreciable oxygen peak. This will often be very much higher than that due to the element being determined. This difficulty can be overcome to some extent by using a derivative circuit and is rendered easier by the absence of any drop wave, which also makes it less serious.

3. Again due to increased sensitivity, the sloping base line due to condenser current and the long drawn out hydrogen peroxide peak cause considerable difficulty in measuring heights at high sensitivity settings.

4. It was found that if a repeat polarogram was run immediately, the peak height had decreased by 10%–20% and further polarograms showed that this effect continued. This was at first attributed to depletion of the solution by deposition into the pool, but on allowing a solution to stand for 30 minutes with no applied potential it was found that the peak height returned very nearly to its original value. It is suggested that the effect may be due to the formation of a very thin layer of amalgam on the surface of the pool; on standing diffusion would take place in the pool and the original conditions would be restored.

CATHODE RAY POLAROGRAPHY

This instrument presents repeat polarograms with each drop using the DME, or every 7 seconds using a pool or solid electrode. With the DME it is necessary to synchronise the voltage sweep and drop time in order to obtain reproducible polarograms. With a pool or solid electrode, this condition no longer applies and reproducible curves are obtained immediately. The preliminary results obtained showed promise, and a comparison of DME and pool cathode was made on this instrument.

The CRP represents a considerable advance over the conventional polarograph, but suffers from some disadvantages when attempts are made to use it with the DME at the limits of its performance.

These disadvantages are as follows:

1. The steep slope to the base line obtained at potentials more negative than about $-0{\cdot}6$ volts, due to condenser current and the hydrogen peroxide peak.

2. The large, rounded rise in current obtained at about −0·4 volts. This has been attributed to the increase in diffusion layer capacity near the electrocapillary maximum.[4]

3. The hum on the trace, which is usually of the order of 5 mm–10 mm at maximum sensitivity, and resembles a sine wave at about 10 c.p.s.–20 c.p.s. This applies to the instrument in our laboratory, and will no doubt vary with the conditions of use. It is not electronic hum, and it is difficult to attribute it to capillary response when only one drop is concerned. The most likely source is vibration, either of the pool anode or the hanging drop, and it is significant that when the electrode stand was mounted directly on a laboratory bench this vibration problem was very much worse. It is possible that the mounting now employed is not completely efficient.

4. The fact that the derivative circuit, which will effectively compensate the steep slope referred to in (1) above, and minimise the effect of the electrocapillary maximum referred to in (2), causes the instrument to lose sensitivity. For most reactions with our instrument this loss in sensitivity is by a factor of about 100, which cannot easily be nullified by further amplification as the hum level is about the same as with the direct circuit.

5. The loss in sensitivity incurred when slow electrode reactions are examined. This loss is often attributed to the irreversibility of the reaction concerned, but in our experience is related in part, at least, to the reaction rate. For example, the reduction of Solochrome Violet RS, a 4-electron irreversible reaction, is one of the most sensitive on the CRP, while the reduction of niobium from EDTA solution at pH 3·05, reported by Ferrett and Milner[5] to be reversible, is a slow reaction and is insensitive.

EXPERIMENTAL

It was hoped that the pool cathode cell would help to overcome some of these difficulties, and in order to assess it against the DME both electrodes were used with 3 reactions. These were:

(i) Cadmium in 0·1*N* KCl, a fast reversible reaction.
(ii) The aluminium complex of Solochrome Violet RS, a fast irreversible reaction.
(iii) Nickel in 0·1*N* KCl, a slow irreversible reaction.

In all cases, a strong solution was used at the beginning, and diluted with distilled water tenfold for the next tests at higher sensitivities, with suitable additions of base electrolyte.

The results obtained are shown in Tables I–III.

TABLE I. CADMIUM IN 0.1*N* KCl

Cd, *ppm*	Peak height, *μA*		Remarks
DME			
10	†1·6		Smooth, ideal polarogram
1·0	0·16		Smooth, ideal polarogram
0·1	0·016*		Marked hum, latter part of trace slopes steeply. Height varied 0·013–0·019 but 0·016 reproduced most often when hum low.
0·01	N.D.*		Peak should be about ½″ in height but lost in ½″ hum on trace.
POOL	Direct	Derivative	
10	100	2·1	Smooth ideal polarogram
1·0	10·0	0·21	Smooth ideal polarogram
0·1	1·1	0·022	Smooth ideal polarogram but O_2 wave present became difficult to compensate
0·01	N.D.	N.D.	Direct wave lost because of steep base line. Derivative wave lost in hum.

* Using maximum sensitivity; full scale = 0·020 μA.

† Derivative wave height 0·0064 using maximum sensitivity.

TABLE II. ALUMINIUM COMPLEX OF SOLOCHROME VIOLET RS

ppm Al	Wave height, *μA*		Remarks
	Direct	Derivative	
DME			
1·0	2·94	0·044	Smooth ideal polarograms
0·1	0·57	*0·0096	Smooth ideal polarograms
0·01	0·075	*0·002	Smooth ideal polarograms
0·001	*N.D.	*N.D.	Direct wave lost "in electrocapillary maximum" followed by steep slope.
POOL			
1·0	24·6	0·29	Smooth ideal polarograms
0·1	4·4	0·065	Smooth ideal polarograms
0·01	1·0	0·023	Smooth ideal polarograms but O_2 wave difficult to compensate.
0·001	0·10	*0·003	Good shape, clean wave on direct. Steeply sloping base line.
0·0001	N.D.	*N.D.	Direct wave lost in steeply sloping base line.

* Using maximum sensitivity.

TABLE III. NICKEL IN 0·1*N* KCl

ppm Ni	Wave height, *μA*		Remarks
	Direct	Derivative	
DME			
10	3·0	0·028	Smooth, unpeaked polarogram
1·0	0·29	*0·002 approx.	Unpeaked polarogram on sloping base line
0·1	0·025 approx.	*N.D.	Unpeaked polarogram on very steeply sloping base line
POOL			
10	62·5	0·40	Smooth, peaked polarogram
1·0	N.D.	0·040	Direct wave merges into Zn wave from KCl
0·1 (0·01 *N* KCl)	N.D.	*0·004	Direct wave merges into Zn wave from KCl Very steeply sloping base line

* Using maximum sensitivity.

REPRODUCIBILITY

The CRP produces polarograms every 7 seconds with a pool cathode. The peak height appears to be reproducible for at least 20–30 sweeps, which is ample time to measure the height. (2–3 sweeps are sufficient.) On standing, however, the peak height changed, and after 1 hour of sweeping every 7 seconds, the height *increased* by about 100%–200%. This is not considered a serious disadvantage, as only the first 2 or 3 sweeps are used for analytical purposes. It is suggested that the reason for this increase as opposed to the decrease obtained with the conventional polarograph is that the pool does not become contaminated to the same extent, as the potential does not remain high for more than about 1 second in every 7. Instead, electromigration slowly takes place, and a more concentrated solution is formed around the cathode. Increasing the concentration of base electrolyte decreases the rate at which the peak current increases, which would appear to lend some support to this theory.

The reproducibility of the cell was checked by measuring the peak heights obtained when several portions of the same lead solution (1 ppm in KCl) were examined, using a new pool each time. 10 results were obtained. The mean value was 4·02 μA; maximum deviations were +0·13 μA and −0·17 μA. Standard deviation was 0·103 μA, = 2·5%.

CONCLUSIONS

(*a*) *Conventional polarography*

The effective gain in sensitivity is by a factor of about 20. The fact that it is not possible to run a repeat polarogram is regarded as a very severe drawback, however, and for this reason alone the use of pool cathode is not recommended with this type of instrument.

(*b*) *Cathode ray polarography*

The pool cathode appears to show some advantages over the DME with this instrument.

The increase in sensitivity, given by the ratio of cell current using the pool to that using the DME is 62·5 for Cd, 8·5 for Al Solochrome and 21 for Ni. No explanation is offered for this discrepancy. The effective gain in sensitivity is not as high as this, however, because the very steeply sloping base line obtained precludes the use of the direct circuit at the highest sensitivities. The derivative circuit benefits most from the use of the pool cathode, as the maximum sensitivity of the instrument can be used, and in many cases the derivative circuit sensitivity becomes as high as the maximum useable direct sensitivity with the DME.

The greatest advantage of the pool cathode cell with the direct circuit is the fact that small concentrations of reducible species can be determined using instrument conditions where the hum level is very low, instead of high sensitivities where the hum is appreciable. In addition, waves occurring at potentials where the base line slope is high can be measured on the derivative circuit without appreciable loss of sensitivity over the direct circuit DME combination. This has the further advantage that close waves can be resolved.

Ultimate usable sensitivity is also increased by a factor of about 10, or slightly more in favourable cases. This may well be nullified by the fact that the CRP in its original form is quite often so sensitive that it is reagent blanks rather than instrument sensitivity that provide the bottom limit of determination.

The disadvantages which remain are the fact that the cells must be individually calibrated, or the same cell used. This is not so serious using the CRP, as the measurements can be made much more quickly than with a conventional instrument.

The CRP will tolerate larger preceding waves than a conventional polarograph, so that the residual oxygen wave is of less importance; the derivative circuit is even better, and will tolerate preceding waves over 500 times as high as the wave being measured.

There is no improvement as regards the absolute value of the hum, but the ionic concentration at which it begins to interfere is lowered. Similarly, there is no improvement in measuring slow reactions other than the overall increase in sensitivity. In spite of these remaining disadvantages, it is felt that the pool cathode cell can offer some advance over the DME when used with the CRP.

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BOOK REVIEWS

A Manual of Paper Chromatography and Paper Electrophoresis. R. J. Block, E. L. Durrum and G. Zweig. Academic Press, Inc., New York: Academic Books Ltd., London. Second edition, 1958. Pp. xi + 710. $12.80.

The object of this book, as stated by the authors, is to present some of the results of the numerous investigations on paper chromatography and paper electrophoresis so that the student may have a sufficient idea of past studies in order to allow him to choose the method which appears to be most promising for the solution of his particular problem. The authors have succeeded in organizing the large amount of material in a convenient manner and the descriptions of methods are readable and explicit.

As in the first edition (1955), this book is divided into two parts. The first part, written by R. J. Block and G. Zweig, is a practical manual on paper chromatography. The second and shorter part by E. L. Durrum is devoted to the practical aspects of paper electrophoresis.

The section of paper chromatography (483 pp.) includes a short chapter on theory, two chapters on general and quantitative methods, ten chapters on specific procedures for various classes of organic compounds, and one chapter on inorganic separations. These procedures include solvent systems for separations, methods of detection of compounds on paper, and other pertinent information.

The section on paper electrophoresis (185 pp.) includes general theory, general and quantitative methods, two-dimensional techniques and continuous flow methods.

The major change from the first edition has been an expansion of the methods to include material published up through 1956 (almost a three-fold increase in references). In view of the rapid growth of these separation techniques in recent years, particularly in the organic and biochemical fields, this new edition serves as an up to date comprehensive manual of methods. As in the past, the authors give the reader the benefit of their judgment and experience by pointing out in some instances those procedures which are recommended.

This book continues to be a valuable addition to any laboratory employing these paper chromatographic or electrophoretic methods.

George H. Morrison

An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry. A. E. Gillam and E. S. Stern; with a foreword by E. R. H. Jones, F.R.S. Second Edition, Edward Arnold (Publishers) Ltd., London, 1958. pp. xi + 326. 50s.

This is not intended to be a text-book for the analyst, and half of its sixteen chapters are concerned with the relations between the structures and light absorption of organic molecules. It gives, however, spectra or spectral data in the ultraviolet and visible regions for some 800 compounds, which may well be of interest to the organic analyst. For the specialist within this field there is a chapter on the detection and identification of carotenoids, anthocyanins, dyes and industrial colours, blood pigments and a number of miscellaneous colourless, but ultraviolet absorbing, substances. Quantitative analysis is considered in two chapters which give examples of various techniques for determining single substances and mixtures, and also in a chapter on miscellaneous applications, where the determination of some physical constants is described. Differential methods are only mentioned.

Where the analyst who uses ultraviolet and visible absorption spectra can well find the book useful is in the more general chapters where the theory and measurement of absorption spectra are clearly and concisely presented. Many such analysts should certainly study the sections on the reliability of photoelectric instruments and the accuracy of quantitative determinations.

There are over 500 references to the literature, amplified by an appendix giving a bibliography of general and absorption spectroscopy. Other appendices give useful information on the absorption characteristics of common solvents and the influence of temperature on absorption measurements of organic compounds. The diagrams are clear and the book is well produced.

David W. Wilson

Modern Manufacturing Formulary. EMIL J. BELANGER. Chemical Publishing Co., Inc., New York. Pp. 399. $10.00.

FOR many of us the word "goldmine" arouses a strong, if somewhat juvenile interest, and this book is described on the dust cover as being a "goldmine of practical formulae and recipes for professional and amateur chemists ... " It is attractively produced, the formulae being in separate sections devoted to food products, flavourings, practical household formulae, cosmetics, medicinal preparations, veterinary remedies, beverages, and miscellaneous. The appendix gives some account of Food and Drug Regulations (U.S.A.), and there is a classified directory of sources of supply (U.S.A.) and a fairly complete index.

The formulae vary from the familiar older type including some "omnibus" mixtures which would defy any analyst, to such things as polystyrene long-wear nylon spray and home-permanent-wave lotions. Very many of the more modern type formulae use materials having trade names, and these names are not distinguished in any way in the text from commonly accepted names. It is rather surprising to find absent, in a "modern" formulary, products such as rust inhibitors, selective weed killers, plant-cutting hormone mixtures, and even antifreeze.

The sources directory, although a fairly full one, would, in places, certainly confuse the amateur. Thus there are headings for boracic acid and borax (different suppliers), but under the heading "boric acid" one is referred to borax. Another heading is "dextrose (cane sugar)".

It is possible that the analyst might find this book of some value in examining a commercial product, although its value, especially outside the U.S.A., is greatly reduced by the extensive use of trade names. One would be interested to know what active constituents one might be expected to encounter in a cough mixture containing "ground life everlasting" as one of the materials from which an infusion is prepared!

A. B. ANGUS

Instrumental Methods of Analysis. H. H. WILLARD, L. L. MERRITT JR. and J. A. DEAN. D. Van Nostrand Co. Ltd., New York and London. Third edition, 1958. Pp. vi + 626. 56s. 6d.

Most analysts interested in instrumental methods will be familiar with the earlier editions of this work in their unusual and rather unwieldy format and they will consequently welcome this third edition, excellently produced in more conventional style and size with a good index.

Each instrumental technique dealt with is first discussed theoretically, generally briefly but nevertheless adequately, so that a proper appreciation of the basic principles involved is gained; then follows a description of typical instruments and principal techniques of application, step by step laboratory instructions for experimental operation, a few questions and problems and finally some selected references.

In addition to the wide range of techniques dealt with in the previous editions, space has now very properly been found for useful introductions to some of the newer methods such as gas chromatography, nuclear magnetic resonance and X-ray fluorescence. In covering the large, heterogeneous and expanding field of analytical instrumentation it is by no means easy to maintain balance and in this volume one feels, that from the students point of view at least, there is some lack of proportion in the very full treatment accorded to, say, flame photometry (40 pages) compared with all other emission spectrographic methods (some 33 pages).

The references selected for further reading are for the most part very judicious but perhaps the European reader may wish to augment the recommendations in a few cases; Courteney Phillips' useful introduction to gas chromatography is referred to in the text (page 349) but the promise that it will be "listed at the end of the chapter" is unfulfilled.

The book has well over 300 illustrations which are generally excellent although the instructional value of some of those depicting little more than instrument consoles may be doubted.

As one of the few texts which attempts to deal with the whole field of instrumental methods of analysis, this reasonably priced, up-to-date volume is definitely to be recommended, although it must be borne in mind that in the instrument description sections, quite naturally, American instruments figure predominantly.

F. J. WOODMAN

Talanta, 1959, Vol. 2, pp. 197 to 200. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The Society for Analytical Chemistry

The eighty-fifth Annual General Meeting of the Society was held on Friday 6 March, 1959, in The Meeting Room of the Royal Society, Burlington House, London, W.1, with the President, Dr. J. H. Hamence, M.Sc., F.R.I.C., in the Chair.

The following Officers and Members of Council were elected for the forthcoming year:—

President: R. C. Chirnside;
Past Presidents serving on the Council: J. H. Hamence, D. W. Kent-Jones, J. R. Nicholls, K. A. Williams;
Vice-Presidents: D. C. Garratt, Magnus A. Pyke, J. G. Sherratt;
Honorary Treasurer: A. J. Amos;
Honorary Secretary: R. E. Stuckey;
Honorary Assistant Secretaries: L. Brealey (Programmes Secretary), S. A. Price.
Other Members of Council: N. L. Allport, H. E. Brookes, R. A. Chalmers, W. T. Elwell, C. H. R. Gentry, J. Haslam, E. I. Johnson, G. W. C. Milner, R. F. Milton, F. C. J. Poulton, T. S. West and C. Whalley.
Ex-officio Members: J. R. Edisbury (Chairman of the North of England Section), A. N. Harrow (Chairman of the Scottish Section), S. Dixon (Chairman of the Western Section), S. H. Jenkins (Chairman of the Midlands Section), F. Holmes (Chairman of the Microchemistry Group), R. A. C. Isbell (Chairman of the Physical Methods Group) and J. I. M. Jones (Chairman of the Biological Methods Group).

After the Annual General Meeting, Mr Chirnside took the Chair and Dr. Hamence delivered his Presidential Address.

Dr. Hamence devoted the major part of his address to the developments that had taken place over the past two years, and devoted the latter part of the address to a limited number of observations on the future course of analytical chemistry.

The fourth Annual General Meeting of the Midlands Section of the Society was held on Tuesday 3 March, 1959, in the Mason Theatre, The University, Edmund Street, Birmingham 3. The Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F., presided.

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

Chairman: Dr. S. H. Jenkins
Vice-Chairman: Dr. H. C. Smith
Hon. Secretary: Mr. G. W. Cherry, 48 George Frederick Road, Sutton Coldfield, Warwickshire.
Hon. Treasurer: Mr. F. C. J. Poulton
Hon. Assistant Secretary: Mr. R. Adkins

The Fifteenth Annual General Meeting of the Microchemistry Group of the Society was held at 6.45 p.m. on Friday 20 February, 1959, at the School of Pharmacy, Brunswick Square, London, W.C.1. By permission of the Dean, the meeting was preceded by visits to the laboratories of the School of Pharmacy.

The Chairman of the Group, D. F. Phillips, F.R.I.C., presided. The Officers and Members of Committee for 1959 are as follows:—

Chairman: Mr. F. Holmes

Vice-Chairman: Mr. C. Whalley

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

Hon Treasurer: Mr. G. Ingram.

Members of Committee: Miss M. Corner, Mr. E. Bishop, Mr. J. A. Hunter, Mr C. A. Johnson, Dr. R. J. Magee and Mr. D. F. Phillips.

The *Hon. Auditors,* Mr. H. Childs and Dr. L. H. N. Cooper, were re-appointed.

The Annual General Meeting was followed by an Ordinary Meeting of the Group, at which Mr. D. F. Phillips gave the Retiring Chairman's Address.

The following meetings have been arranged:

Monday–Tuesday 6–7 *April* 1959: **Chemical Institute of Canada,** Analytical Chemistry Division, Eighth Regional Conference. Symposium: *Instrumental Methods of Analysis.* Information from J. D. SANDS, Polymer Corporation, Ltd., Sarnia, Ontario, Canada.

Monday–Saturday 6–11 *April* 1959: **International Union of Pure and Applied Chemistry:** International Conference on *Coordination Chemistry.* Information from The Chemical Society, Burlington House, Piccadilly, London, W.1, England.

Wednesday 8 *April* 1959: **Royal Institute of Chemistry,** Mid Southern Counties Section: **Society for Analytical Chemistry,** Western Section. Visit to works of Tintometer Ltd. *Advantages and Disadvantages of Visual Colorimetry:* G. J. CHAMBERLIN. Cathedral Hotel, Salisbury, Wilts, England. 7.45 p.m. (Works visit 5.30 p.m.)

Wednesday 8 *April* 1959: **Society for Analytical Chemistry,** Microchemistry Group. Review Discussion Group, "The Feathers", Tudor Street, Bouverie Street, Fleet Street, London, E.C.4, England. 6.30 p.m.

Thursday 9 *April* 1959: **Society for Analytical Chemistry,** Midlands Section: *Analytical Chemistry in Glass Manufacture:* J. DAVIES, The University, Birmingham, 3, England. 6.30 p.m.

Saturday 11 *April* 1959: **Society for Analytical Chemistry,** North of England Section: *The Training of Analytical Chemists:* G. F. LONGMAN, B.Sc., F.R.I.C. City Laboratories, Mount Pleasant, Liverpool, England. 2.15 p.m.

Wednesday 15 *April* 1959: **Society for Analytical Chemistry,** Scottish Section: *The Analytical Chemistry of Some of the Lower Phosphorus Oxyacids:* Dr. D. S. PAYNE. A.R.C.S., A.R.I.C. *Qualitative Analysis by Solvent Extraction Methods:* Dr. R. A. CHALMERS and D. M. DICK, B.Sc. Central Hotel, Glasgow, Scotland. 7.15 p.m.

Thursday 16 *April* 1959: **Society for Analytical Chemistry,** Biological Methods Group: *Problems of Recording and Communicating Technical Information in a Commercial Research Organisation:* PAMELA D. WATERHOUSE. "The Feathers", Tudor Street, Bouverie Street, Fleet Street, London, E.C.4. 6.30 p.m.

Thursday 30 *April* 1959: **Society for Analytical Chemistry,** Midlands Section: Works Visit and Lecture: *Quality Control in a Pharmaceutical Organisation:* DR. D. C. GARRATT, F.R.I.C. Boots Pure Drug Co., Ltd., Nottingham, England. 12.30 p.m.

Friday 8 *May* 1959: **Royal Institute of Chemistry,** South Wales Section: **Society for Analytical Chemistry,** Western Section and Microchemistry Group: *Rock and Mineral Analysis and Geochemical Prospecting.* Swansea, South Wales.

Monday–Wednesday 18–20 *May* 1959: **Instrument Society of America:** Fifth National Symposium on *Instrumental Methods of Analysis.* Houston, Texas, U.S.A. Information from M. D. WEISS, Union Carbide Olefins Co., South Charleston, W. Va., U.S.A.

Monday–Thursday 1–4 *June* 1959: **American Association of Spectrographers:** Tenth Annual Symposium on Spectroscopy. Conrad Hilton Hotel, Chicago, Ill. Information from H. M. WILSON, Continental Can Co., 7622 So. Racine Ave., Chicago, 20, Ill., U.S.A.

Wednesday–Friday 10–12 *June* 1959: **American Chemical Society,** Division of Analytical Chemistry, and *Analytical Chemistry:* 1959 Summer Symposium: *Complex Reactions in Analytical Chemistry.* University of Illinois. Information from G. L. CLARK, University of Illinois, Urbana, Ill., U.S.A.

Wednesday–Friday 10–12 *June* 1959: **Instrument Society of America:** Second International Symposium on *Gas Chromatography.* East Lansing, Michigan. Information from H. S. KINDLER, ISA, 313 Sixth Avenue, Pittsburgh, 22, Pa., U.S.A.

Tuesday–Tuesday 1–8 *September* 1959: **Czechoslovak Chemical Society of the Czechoslovak Academy of Sciences:** Third International Conference on Analytical Chemistry, Prague. Review and discussion of *The Current State of Analytical Chemistry.* For the participants, and especially for foreign visitors, visits to university laboratories and industrial research centres, and cultural programmes will be arranged. From *Tuesday* 8 *September* to *Friday* 11 *September* an International Pharmaceutical Congress will take place in Karlovy Vary (Czechoslovakia) so that participants in the Analytical Conference could also take part in this.

Information from Dr. JAROSLAV ZÝKA, Department of Analytical Chemistry, Charles University, Praha, II, Albertov 2030, Czechoslovakia.

Revised British Standards have been published as follows:

B.S. 903: *Methods of testing vulcanised rubber.* **Part B19: 1958:** *Preparation and examination of water extract* (replacing **Part 12** in **B.S. 903: 1950)** Price 3s.

This covers the preparation of the water extract and the following tests: Total water soluble material, electrical resistivity, free acid or free alkali, pH value, chloride, sulphate, ammonium salts.

B.S. 1016: *Methods for the analysis and testing of coal and coke:* **Part 6: 1958.** *Ultimate analysis of coal.* Price 10s.

This deals with the determination of carbon, hydrogen, nitrogen and sulphur in coal.

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

BOOKS RECEIVED

Colorimetric Intermination of Traces of Metals, 3rd ed. E. B. SANDELL. Interscience Publishers Inc. New York, $24.00.

Precipitation from Homogeneous Solutions. L. GORDON, M. L. SALUTSKY and H. H .WILLARD. John Wiley & Sons Inc., New York, 1959. Pp. viii + 187.

Gas Chromatographie. A. I. M. KEULEMANS, transl. E. CREMER. Verlag Chemie, Weinheim, 1959. Pp. xvi + 208. DM. 24.

Tables of Constants and Numerical Data, Vol. 8. Selected Constants: Oxidation-Reduction Potentials. G. CHARLOT. Pergamon Press, London, New York, Paris, 1958. Pp. vi + 41. 30s.

Chemistry of the Co-ordinate Compounds. International Series of Monographs on Inorganic Chemistry, Vol. I. Edited by H. TAUBE and A. G. MADDOCK. Rome Symposium, 15–21 September, 1957. Pergamon Press, London, New York, Paris, 1958. Pp. 638. L5.

EDTA Titrations: An Introduction to the Theory and Practice. H. FLASCHKA. Pergamon Press, London, New York, Paris, 1959. Pp. 138. 42s.

Wednesday–Friday 10–12 *June* 1959: **American Chemical Society,** Division of Analytical Chemistry, and *Analytical Chemistry:* 1959 Summer Symposium: *Complex Reactions in Analytical Chemistry.* University of Illinois. Information from G. L. CLARK, University of Illinois, Urbana, Ill., U.S.A.

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Gas Chromatographie. A. I. M. KEULEMANS, transl. E. CREMER. Verlag Chemie, Weinheim, 1959. Pp. xvi + 208. DM. 24.

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EDTA Titrations: An Introduction to the Theory and Practice. H. FLASCHKA. Pergamon Press, London, New York, Paris, 1959. Pp. 138. 42s.

PAPERS RECEIVED

Argentometrische Titrationen mit Redoxindikation—II. Bestimmung von Ammoniak, Ammonium. Ionen und stickstoffhaltigen organischen Substanzen. L. ERDEY, K. VIGH and L. POLOS. (1 *January* 1959.)

Argentometric Titrations with Redox Indicators—III. Determination of Nitrate Ions and Nitro Compounds. L. ERDEY, L. POLOS and Z. GREGOROWICZ. (2 *January* 1959.)

Untersuchung von als Redoxindicatoren Anwendbaren Variaminblauderivaten. L. ERDEY, E. BANYAI und E. B.-GERE. (2 *January* 1959.)

Analytical Applications of Xylenol Orange—II. Spectrometric Study of the Zirconium Xylenol Orange Complex. K. L. CHENG. (17 *January* 1959.)

Studies on Oxygen Determination in Organic Microanalysis—I. A Modified Purification Method for Nitrogen Gas. SATOSHI MIZUKAMI, TADAYOSHI IEKI and KAZUE NUMOTO. (26 *January* 1959.)

Studies on Oxygen Determination in Organic Microanalysis—II. The Microanalysis of Oxygen by the Decrease in the Quantity of Anhydroiodic Acid. SATOSHI MIZUKAMI and TADAYOSHI IEKI. (26 *January* 1959.)

Direkte komplexometrische Eisenbestimmung mit Xylenolorange als Indikator. F. VYDRA, R. PŘIBIL und J. KORBL. (27 *January* 1959.)

Metalfluorechromic Indicators. D. H. WILKINS. (28 *January* 1959.)

The Determination of Conductivities using Unconventional Electrode Systems. V. S. GRIFFITHS. (27 *January* 1959.)

On the Heterolytic and Homolytic Dissociation of Bromine Chloride and on the Determination of the Bromine Formed during Homolytic Dissociation. E. SCHULEK and K. BURGER. (9 *February* 1959.)

The Detection of Carbon in Spot Test Analysis. ALCIDES CALDAS and VICENTE GENTIL. (18 *February* 1959.)

The Determination of vic-Dioximes. CHARLES V. BANKS and JOHN J. RICHARD. (25 *February* 1959.)

The Effect of Absorbancy upon Raman Intensities in Solution. FREDERICK VRATNY and ROBERT B. FISCHER. (4 *March* 1959.)

Spectrophotometric Determination of Palladium with Thiomalic Acid. VERNON L. WAGNER, Jr. and JOHN H. YOE. (27 *February* 1959.)

Benzidine and Derivatives in Analytical Chemistry. S. J. LYLE. (5 *March* 1959.)

Spectrophotometric Determination of Ruthenium with N:N′-bis-(3-Dimethylaminopropyl)-dithiooxamide. WILLIAM D. JACOBS and JOHN H. YOE. (10 *March* 1959.)

Spectrophotometric Determination of Rhodium with Thiomalic Acid and the Simultaneous Determination of Rhodium and Palladium. VERNON L. WAGNER, Jr. and JOHN H. YOE. (12 *March* 1959.)

A Transistorised Drop-Counter for Chromatographic Use. G. GEERINCK and J. HOSTE. (13 *March* 1959.)

Le Séparation Niobium-Tantale en Milieu Chloro-Oxalique sur Échangeur D'Anions. A. SPEESKE and J. HOSTE. (13 *March* 1959).

Direct-Reading Current Integrator for Coulometric Analysis. SHIGEKI HANAMURA. (13 *March* 1959.)

A Critical Evaluation of Spectrographic, Fluorescent X-Ray and Polarographic Methods for the Determination of the Platinum Metals. F. E. BEAMISH. (13 *March* 1959.)

Co-ordination of the NO Group in Hexa-co-ordinated Iron Compounds. D. J. MORGAN. (18 *March* 1959.)

Rapid Method for Coulometric Analysis using an I-Q Recorder. SHIGEKI HANAMURA. (19 *March* 1959.)

Talanta, 1959, Vol. 2, pp. 201 to 208. Pergamon Press Ltd. Printed in Northern Ireland

THE DETERMINATION OF COPPER WITH TRIETHYLENETETRAMINE USING A METALFLUORECHROMIC INDICATOR

DONALD H. WILKINS and LOUIS E. HIBBS
General Electric Research Laboratory, Schenectady, New York, U.S.A.

(*Received* 3 *October* 1958)

Summary—Triethylenetetramine (trien) has been applied as a selective titrant for the determination of copper without separations or masking of many elements normally found in brasses and bronzes.

The application of a metalfluorechromic indicator has made possible the use of trien for the determination of macro amounts of copper without resort to an instrumental end-point detection method.

Calcein W serves as a selective indicator for copper in the presence of many elements normally found in brasses and bronzes.

THE wide application of ethylenediaminetetra-acetic acid (EDTA) and nitrilotriacetic acid in chelometric titrations has not been extended to include polyamines. In contrast to the voluminous literature applying EDTA to inorganic analytical problems only two papers have appeared using triethylenetetramine as a chelometric reagent.[1,2]

In order to be useful as a titrimetric reagent in a chelometric titration, a polyamine must form a complex with a metal ion sufficiently stable to provide a sharp end-point in a titration. In general, this necessitates the formation of a stable 1 : 1 complex between the metal ion and the chelating agent ($pK > 8$). The actual stability constant is not as important as the apparent stability constant as has been adequately demonstrated by Schwarzenbach.[3] Theoretical titration curves have been calculated for triethylenetetramine and copper[4] as well as a theoretical treatment of the titration of pure copper solutions.[5]

The actual stability constants of several polyamines have been accumulated.[6] Of these, three appear promising as titrimetric reagents: 2:2′:2″-triaminotriethylamine, triethylenetetramine, and N:N:N′:N′-tetrakis-(2-aminoethyl)-ethylenediamine. Fortunately the selection of a suitable polyamine for a volumetric titration can be made with a few relatively simple calculations.

The polyamines may be treated as polybasic acids; as such the acidity constants may be expressed mathematically as follows:

$$K_1 = \frac{[H_4B^{+4}]}{[H^+][H_3B^{+3}]} \qquad K_3 = \frac{[H_2B^{+2}]}{[H^+][HB^+]}$$

$$K_2 = \frac{[H_3B^{+3}]}{[H^+][H_2B^{+3}]} \qquad K_4 = \frac{[HB^+]}{[H^+][B]}$$

for example for triethylenetetramine. The concentration of the polyamine present in solution is equal to the sum of the ionic species of the polyamine

$$C = [B] + [HB^+] + [H_2B^{+2}] + [H_3B^{+3}] + [H_4B^{+4}] \tag{1}$$

where C is the total concentration of triethylaminetetramine not bound to the metal and the members on the right hand side of equation (1) are the various ionized species of the polyamine. The expressions for the four ionization constants may be rearranged so as to place the undissociated species in each expression on the left side of the equation and, by substitution, from the preceding equation (2 to 5) each species is expressed in terms of the completely ionized form (designated as B).

$$[HB^{+}] = [H^{+}]K_4[B] \tag{2}$$

$$[H_2B^{+2}] = [H^{+}]K_3[HB^{+}] = [H^{+}]^2K_4K_3[B] \tag{3}$$

$$[H_3B^{+3}] = [H^{+}]K_2[H_2B^{+2}] = [H^{+}]^3K_4K_3K_2[B] \tag{4}$$

$$[H_4B^{+4}] = [H^{+}]K_1[H_3B^{+3}] = [H^{+}]^4K_4K_3K_2K_1[B] \tag{5}$$

The equivalent values for the various ionized species from equations (2) to (5) may be substituted into equation (1).

$$C = [B] + [H^{+}]K_4[B] + [H^{+}]^2K_4K_3[B] + [H^{+}]^3K_4K_3K_2[B] + [H^{+}]^4K_4K_3K_2K_1[B] \tag{6}$$

Equation (6) may be rearranged in a manner more convenient for the calculation of apparent stability constants of metal-triethylenetetramine complexes.

$$[B] = \frac{[C]}{1 + [H^{+}]K_4 + [H^{+}]^2K_4K_3 + [H^{+}]^3K_4K_3K_2 + [H^{+}]^4K_4K_3K_2K_1} = \frac{[C]}{\alpha_H} \tag{7}$$

The term designated by α_H has been derived in a more generalized manner and applied to theoretical considerations of chelometric titrations with ethylenediaminetetra-acetic acid and nitrilotriacetic acid by Schwarzenbach.[3]

The actual stability constant for the reaction between a metal ion and polyamine may be expressed as follows:

$$K = \frac{[MB]}{[M][B]} \tag{8}$$

where [M] is the concentration of metal ion not complexed with the polyamine and [B] is concentration of the free polyamine. Substitution of the value for [B] from equation (7) into equation (8) gives the expression for the apparent stability constant K_a.

$$K_a = \frac{K}{\alpha_H} = \frac{[MB]}{[M][C]} \tag{9}$$

Equation (9) is useful to compare the apparent stability of several polyamine complexes. The α_H term, derived above for triethylenetetramine, may be derived for other polyamines and a first approximation may be obtained concerning their relative merits as titrants. For example Fig. 1 shows the variation with pH of log α_H for triethylenetetramine, 2:2′:2″-triaminotriethylamine, and N:N:N′:N′-tetrakis-(2-aminoethyl)-ethylenediamine (hereafter referred to as trien, tren, and penten respectively).[4] The application of this mathematical treatment of the effect of pH on the apparent stability of the complexes of copper with polyamines is more obvious if the logarithm of the apparent stability constant is plotted as a function of pH (Fig. 2). The curves in Fig. 2 were obtained by subtracting log α_H from log K_{Cu}. It is obvious from Fig. 2 that at a low pH trien is the most effective complexing agent for copper.

The minimum value of the apparent stability constant which will allow a successful titration must be determined in a somewhat arbitrary manner. A rigorous treatment of this value must include the concentration of the metal being titrated, the presence of auxiliary complex formers (for example, buffers), the tolerable titration error, etc., and is beyond the scope of this article.

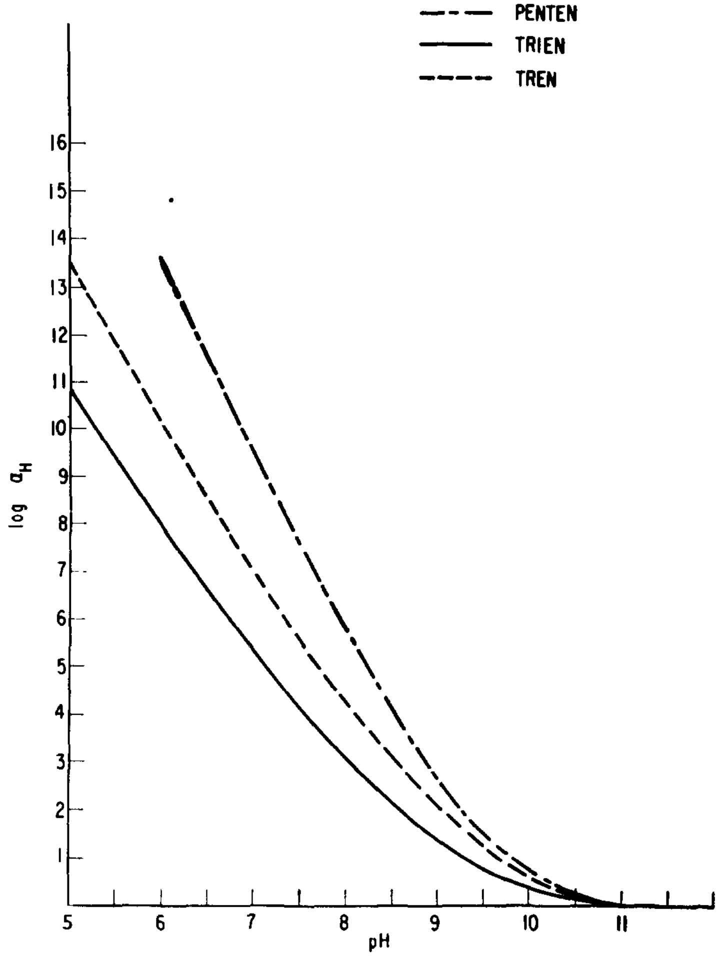

FIG. 1. Log α_H *vs.* pH for three polyamines.

An additional criterion which must be considered, however, is the availability of the reagent. Triethylenetetramine (trien) is available commercially (although impure) whereas tren and penten must be prepared in the laboratory by somewhat laborious procedures.

The mathematical treatment presented above indicated that tren and penten have no advantages over the trien for the determination of copper. On this basis triethylenetetramine was selected as a suitable titrant. It should be mentioned, however, that the larger apparent stability of the penten copper complex at a high pH could prove advantageous for microtitrations.

Previous investigations of the use of trien to titrate copper[1,2] have recommended instrumental methods for detecting the end-point. The titration of copper using murexide as an indicator is limited to less than 0.05 millimoles of copper because of the intense blue colour of the copper-polyamine complex.[2] The introduction of metalfluorechromic indicators has eliminated many of the difficulties previously encountered in chelometric titrations in which the colour of the metal-EDTA complex interfered with the colour change at the end point.

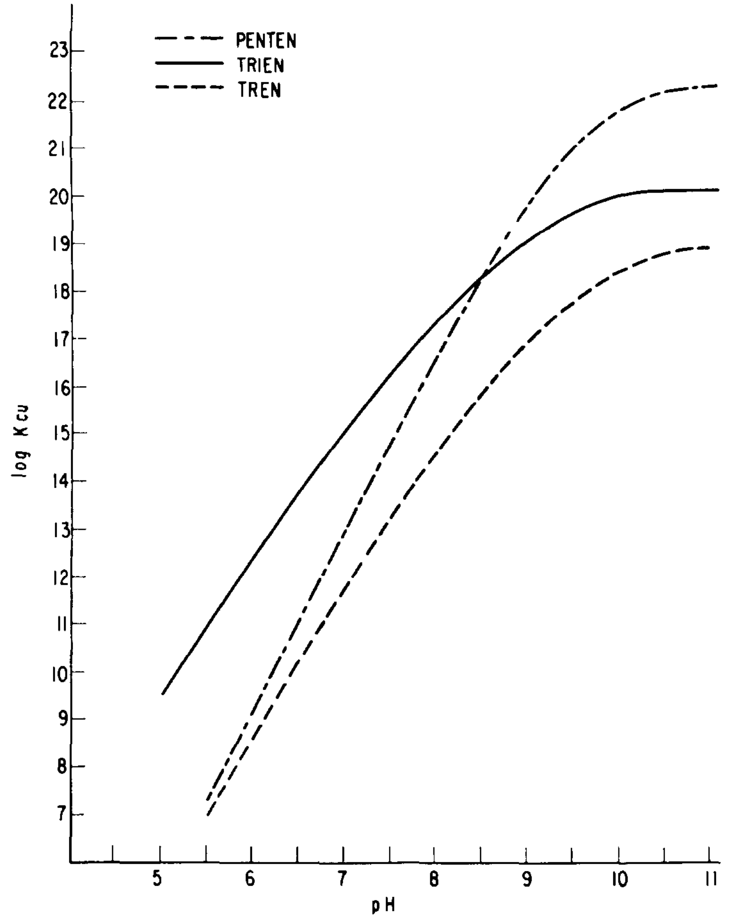

Fig. 2. Logarithm of the apparent stability constant of the copper-polyamine complex *vs.* pH for three polyamines.

The successful application of calcein as a metalfluorechromic indicator for back titrations of EDTA with a copper solution[7] suggested that a similar technique would provide a suitable indicator for the titration of copper with triethylenetetramine. A copper solution was prepared and standardized with EDTA. Aliquots were taken to contain from one to sixty mg of copper and were titrated with triethylenetetramine using calcein W as an indicator under ultraviolet light. The end-point is characterized by the appearance of the green fluorescence of the free indicator. Dropwise addition of the titrant near the end-point produces a fluoresence where the drop enters the solution. This fluoresence with the local excess of titrant disappears with stirring in the same manner as with conventional indicators. At the end-point a single drop of titrant produces a brilliant fluoresence throughout the solution. The results obtained by titrating pure copper solutions with trien using calcein W as an indicator under ultraviolet illumination are presented in Table I.

It is apparent from the stability constants that some metals form more stable complexes with trien than others.[6] This fact introduces the possibility of titrating copper in the presence of elements which do not form particularly stable ammine complexes such as calcium, magnesium, manganese, etc. The possibility of performing such titrations is more apparent from a plot of the apparent stability constant *vs.* pH (Fig. 3). Copper has been determined in an aluminum alloy by titrating with trien using a spectrophotometric end-point.[1] An examination of Fig. 3 indicates that the determination of copper with trien should be possible in the presence of other elements with a suitable end-point detection method. Although spectrophotometric and potentiometric methods are possible, it is more desirable for routine analysis to use a visual indicator.

TABLE I. TITRATION OF PURE COPPER SOLUTIONS WITH TRIEN

mg Cu present	*mg* Cu found	pH
19.06	19.10	7
19.06	19.06	7
19.06	19.08	7
19.06	19.06	7
38.12	38.03	7
38.12	38.11	7
38.12	38.05	7
38.12	38.17	7
57.18	57.10	7
57.18	57.19	7
76.24	76.06	7
76.24	76.18	7
19.06	19.11	9.5
19.06	19.09	9.5
19.06	19.05	9.5
19.06	19.05	9.5

An investigation was initiated into the possibility of using calcein W as an indicator for the determination of copper with trien in the presence of manganese and zinc. Preliminary investigations revealed that manganese and zinc do not quench the fluorescence of calcein W in a solution buffered to a pH of 7 with ammonium acetate. The magnitude of the apparent stability constant (Fig. 3) of the copper complex compared to those of manganese and zinc suggest that copper (in the presence of manganese or zinc) will be essentially completely titrated with trien before an appreciable amount of trien-manganese or trien-zinc complex is formed.

Solutions of manganese and zinc were prepared and added to measured aliquots of the standard copper solution. The solution was adjusted to a pH of 7 by the addition of solid ammonium acetate, one drop of calcein W solution was added and the solution titrated with trien under ultraviolet illumination to the appearance of the green fluorescence of the free indicator. The results of these titrations are shown in Table II.

The determination of copper in the presence of zinc and manganese suggests the feasibility of developing a procedure for the rapid determination of copper in brasses and bronzes. In order to verify such a procedure a National Bureau of Standards sample (No. 164) was selected and copper determined using the procedure given below.

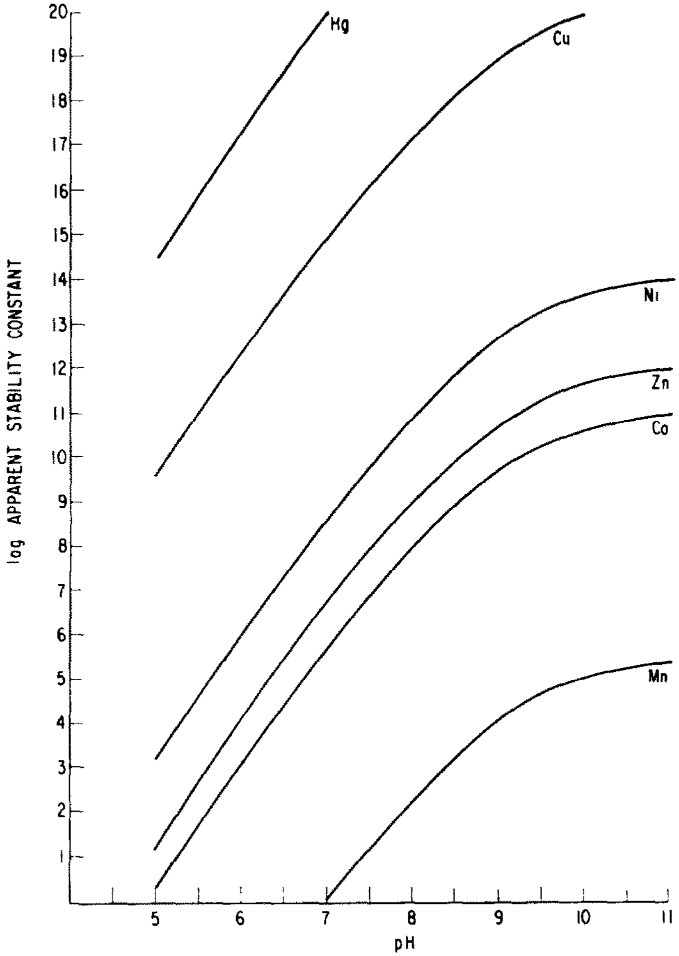

FIG. 3. Logarithm of the apparent stability constant of several metal-trien complexes *vs.* pH.

Procedure

Dissolve a 0.5-g sample in 3 ml of water, 1 ml of nitric acid and 10 drops of hydrochloric acid. After dissolution transfer the sample solution to a 100-ml volumetric flask and dilute to volume with water. Add 100 ml of water, 3 g of ammonium acetate and 5 drops of calcein to a 10-ml aliquot in a 250-ml beaker. Titrate the copper with a standard trien solution which has been adjusted to a pH of 7 (pH paper) before standardization. The end-point is characterized by the appearance of the green fluorescence of the free indicator. The values in Table II designated sample number 164 and 52c were determined by the procedure described above.

DISCUSSION

The titrations of the standard copper solutions and the brass sample were conducted using ultraviolet lamps as the sole source of illumination. An apparatus designed for fluorescent titrations has been previously described.[7]

An interesting development in the application of metalfluorechromic indicators to chelometric titrations is found in the fact that several of the titrations presented in Tables I and II were performed by an individual who is colour blind (blue-green). Thus, in addition to eliminating interferences from highly coloured complexes, metalfluorechromic indicators may be used in instances where the operator is unable to detect the colour changes of conventional indicators.

TABLE II. TITRATION OF COPPER IN PRESENCE OF OTHER ELEMENTS WITH TRIEN

Sample No.	*mg* Cu present	*mg* Cu found	Second element present *mg*
1	19.06	19.07	10 Mn
2	19.06	19.00	10 Mn
3	19.06	18.95	10 Mn
4	19.06	18.97	10 Mn
5	19.06	19.07	10 Mn
6	19.06	19.01	10 Mn
7	19.06	19.03	10 Zn
8	19.06	18.99	10 Zn
9	19.06	19.03	10 Zn
10	19.06	18.97	10 Zn
164–1	32.42	32.37	NBS Bronze No. 164*
164–2	32.42	32.42	NBS Bronze No. 164*
164–3	32.42	32.42	NBS Bronze No. 164*
164–4	32.42	32.37	NBS Bronze No. 164*
164–5	32.06	32.16	NBS Bronze No. 164*
164–6	32.06	31.92	NBS Bronze No. 164*
164–7	32.06	32.11	NBS Bronze No. 164*
52c–1	41.89	41.75	NBS Bronze No. 52c*
52c–2	41.89	41.75	NBS Bronze No. 52c*
52c–3	41.89	41.78	NBS Bronze No. 52c*

* 52c 89.25 Cu, 7.85 Sn, 2.12 Zn, 0.76 Ni, 0.011 Pb, 0.004 Fe

* 164 63.76 Cu, 21.89 Zn, 6.21 Al, 4.68 Mn, 2.52 Fe, 0.63 Sn, 0.22 Pb, 0.046 Ni

It should be noted that the procedure for the determination of copper in brasses and bronzes is dependent on the fact that the indicator is not blocked by elements present in the sample. The procedure will not work at a pH of 9 since the fluorescence of calcein W is quenched by other elements at this pH. A more exhaustive study is in progress to determine the properties of calcein W as an indicator for elements other than copper.

Commercial trien should be purified before it is used as a titrant. A procedure for its purification by precipitating the sulphate has been described.[2]

Calcein W is preferable to calcein for fluorescent titrations. Both are a condensation product of fluorescein, formaldehyde and iminodiacetic acid, but calcein W is not contaminated with unreacted fluorescein. Fluorescein gives a fluorescence which is not quenched by copper and the residual fluorescence causes some difficulty when the procedure is applied to a brass such as NBS 164 or 52c.

Zusammenfassung—Es wurde die Anwendung von Triäthylentetramin (Trien) zum Titrieren von Kupfer beschrieben. Ein Metallfluorochromatischer Indikator, Calcein W, wurde angewandt. Die Bestandteile der Kupferlegierungen (Bronce und Messinge) üben keine Wirkung auf die Bestimmung aus.

Résumé—Les auteurs ont utilisé la triéthylène triamine (trien), comme réactif titrant sélectif pour le dosage du cuivre sans séparation ou dissimulation des nombreux éléments présents normalement dans les laitons et les bronzes.

L'application d'un indicateur "metalofluorochromique" a rendu possible l'utilisation de la "trien" pour le dosage de très grandes quantités de cuivre sans recourir à une méthode instrumentale pour la détermination du point équivalent.

La "calceine W" sert comme indicateur sélectif pour le cuivre en présence des nombreux éléments que l'on trouve normalement dans les bronzes et les laitons.

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WET OXIDATION OF ORGANIC MATTER EMPLOYING MIXED PERCHLORIC AND SULPHURIC ACIDS AT CONTROLLED TEMPERATURES AND GRADED HIGH POTENTIALS

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Summary—The oxidation potential of perchloric acid at the boiling point is a function of temperature and concentration. At ordinary temperature no oxidation potential is provided in the concentration range 0 to 73.6%. At its boiling temperature 50% perchloric acid fails to oxidize Fe^{II} except very slowly. At 72.5% acidity, (the azeotropic concentration), the boiling acid, (203°), is a strong oxidant. For example Cr^{III} is easily oxidized to CrO_3. Between concentrations of 50% to 72.5%, the boiling acid provides oxidation potentials of continuously mounting values. By control of suitable desired concentrations through boiling under reflux, many practical procedures may be devised for the controlled wet oxidations of organic compositions.

For higher oxidation potentials, higher concentrations of perchloric acid are required. By the addition of concentrated sulphuric acid in various ratios by volume to 70% perchloric acid, effective concentrations of the latter may be provided up to and including 100%. Again by control of the particular concentrations of the mixed acids selected, through boiling under reflux, extremely high graded oxidation potentials, under static control, may be provided.

The use of sulphuric acid in such applications serves the additional important function of tempering the reaction and controlling reaction rates. The addition of 1 to 2 mg of vanadium as reaction catalyst serves the same purpose. Vanadium also favorably influences the reaction kinetics while shortening the oxidation period required.

Procedures making use of these reaction variables are herein experimentally demonstrated. The wet oxidation of such samples as coal, ion-exchange resins, alkaloids, synthetic fabric materials, rubber, heterocyclic ring nitrogen compounds and other materials serve as examples. No hazardous reactions were encountered in this work.

INTRODUCTION

THE preparation of macro-weight samples of natural and artificially prepared organic compositions for the determination of metallic and non-metallic elements, either principal constituents or trace-element ingredients, involves the oxidation of the organic matter as a preliminary operation. Two general type procedures are employed: dry ashing, or wet ashing. The use of perchloric acid, or its mixtures with nitric or sulphuric acid, has in great measure replaced dry ashing procedures and also the use of other reactants for wet ashing techniques.

For the wet ashing methods requiring the application of the highest available oxidation potential, the use of mixed perchloric and sulphuric acids is required. The present work deals with this general problem. The variable factors governing the magnitude of the oxidation potential attainable, and illustrative procedures in the wet oxidation of organic compositions most resistant to oxidation are provided.

PREVIOUS APPLICATIONS

The mixed oxidants, nitric and perchloric acids have been extensively applied in wet oxidation procedures.[1] The fields of application have been foods, feeds, biological materials, leather, paper and paper pulp, wine, fuels, powdered dry milk and buttermilk, as well as blood and blood fibrin[2] and other materials.

The use of perchloric acid alone at graded oxidation potentials and controlled temperatures, has been applied to compositions essentially of cellulose, proteins, and sugars.[3]

The application of mixed perchloric and sulphuric acids in the wet oxidation of animal feeds and fæces has been extensively employed as described by Bolin and Stamberg.[4] Molybdenum was added as reaction catalyst. This process has been adapted to the determination of Eden's Indicator Method for evaluation of "digestive coefficient" using chromic oxide as indicator and is widely used in animal feeding experiments.

An extensive accumulation of literature references is found by examination of these publications. Techniques in the use of dry ashing procedures, applied almost exclusively in the field of millimicrogram trace-element determinations, has been described by Thiers.[5]

BASIC REACTION CHARACTERISTICS

By the use of mixed perchloric and sulphuric acids at elevated temperatures, the effective concentration of perchloric acid made available is conveniently altered. The concentration range made available is from 70% to 100%. By addition of sulphuric acid, the rate of oxidation of organic matter is tempered by its dilution effect. The dehydration of 70% perchloric, as by addition of concentrated sulphuric acid, accounts for the increase in effective perchloric acid concentration.

By proper selection of the governing proportions of concentrated sulphuric and 70% perchloric acid, and by providing means to maintain the original concentration of reaction ingredients, a wide range of available oxidation potentials is made readily available. By the addition of pre-determined portions of water to the mixed oxidants, and with suitable control in maintenance of the original reactants, potentials from moderate to maximum values may be rigidly established.

By the use of vanadium in milligram amounts, the time interval required for a given wet ashing oxidation is markedly shortened. Provision for ready alteration of reactant concentrations during a given digestion adds to the versatility of the process and widens its scope.

APPARATUS DESIGN

The Bethge digestion apparatus[6] is admirably designed to control reaction conditions. A line drawing is shown in Figure 1.

A Rogers ring burner[7] and plain Nichrome wire gauze upon which the Bethge digestion flask is mounted, serves to provide a readily controlled heat supply. The reaction flask may be 125-, 250- or 500-ml volume with a 24/40 \$ ground joint opening. The reaction flask, only, requires a clamp support. The air-cooled condenser provided with \$ ground joints at top and bottom as shown has a three-way lower stopcock terminal. Through its setting, provision is made for either the return or retention of flask distillate. The water-cooled condenser is held firmly in place at the ball and socket union with the air-condenser by a standard clamp.

At the completion of a reaction of wet oxidation, the apparatus is conveniently disassembled and both the water-condenser and air-condenser placed on the side. A suitable sturdy screw pinch-clamp is provided over the tubing connecting the Rogers ring burner to the gas supply. By its use the heat may be discontinued more conveniently between reactions or during reaction. The setting of the gas supply is adjusted at the base of the burner with micro-control. Provision is made for regulation in the height of the reaction flask on the wire gauze support above the ring burner gas flame. No lubricant other than perchloric acid is required for all glass joints.

It is not a prerequisite, but a sensible precaution, to provide a shield of 6-mm Lucite 30 to 40 cm square mounted on suitable metal supports to place between the operator and the reaction flask. The reaction flask should be provided with a thermometer-well and 250° thermometer. By its use control of reaction rates and designation and detection of exothermic reaction stages may be accurately noted.

A stop-watch is appropriate for tabulation of reaction intervals and temperatures. With reactants added to the flask, the water and air-condenser are mounted in place with the stopcock set to return reflux to the digestion flask. By this means the reaction oxidant may be maintained for the entire period of reaction practically unaltered in composition. If desired the air-condenser stopcock may be altered. This results from the distillation of aqueous perchloric acid, with corresponding alteration of the effective ratio of sulphuric to perchloric acids in the reacting oxidants.

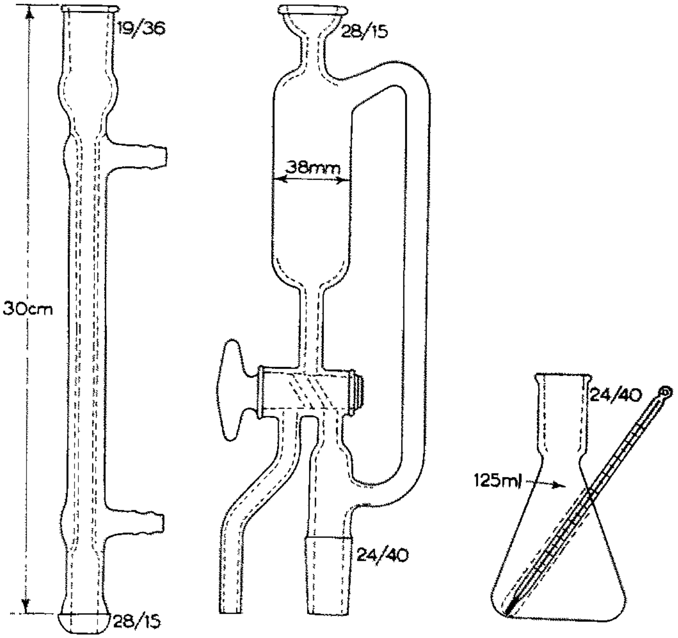

FIG. 1.

During the progress of a given digestion reactants may be added through the water-condenser. Reaction catalyst may be added by this process at any time interval during a given digestion.

MIXED PERCHLORIC AND SULPHURIC ACIDS AS OXIDANTS

For the lower magnitude oxidation potentials, concentrated sulphuric (96.3%) and perchloric (69.6%) acids, with added water, in various proportions are applicable. The boiling point of a series of such mixtures is given by reference to the data shown in Figure 2. The higher the boiling point the greater the potential provided.

For various mixtures of the same concentrated acids without added water, the effective concentrations of perchloric acid produced upon boiling are shown in the data of Figure 3. For these data, a 0.5- to 1-ml volume of distillate from the boiling mixed acids was collected and the concentration of perchloric acid determined. The boiling point, with some little decomposition, was between 212° and 216°. The formation of chlorine and oxides of chlorine as degradation products of perchloric acid was noted.

By examination of the data of Figure 3, it is seen that the effective concentration of perchloric acid provided is up to and including the anhydrous strength.

From the data of Figures 2 and 3 it is thus obvious that provision is made for establishing, and maintaining, controlled oxidation potentials covering a wide range of stepwise increasing magnitude.

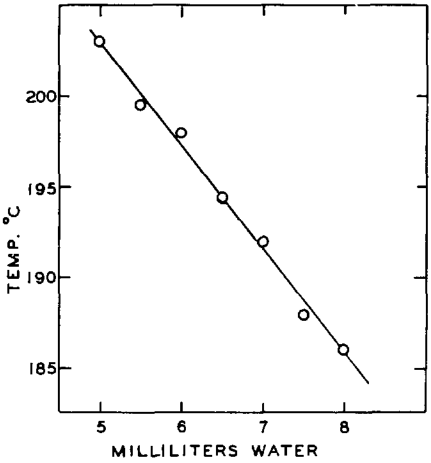

FIG. 2.

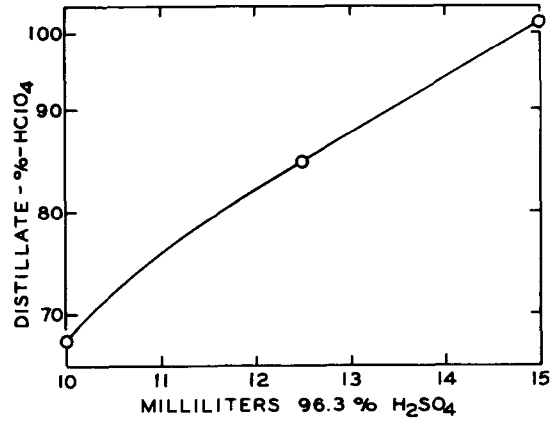

FIG. 3.

PREVIOUS APPLICATIONS OF PERCHLORIC-SULPHURIC ACIDS IN THE DESTRUCTION OF ORGANIC MATTER

The early use of hot concentrated sulphuric acid in the destruction of organic matter, with the use of perchloric acid additions as accelerator, were employed by Gauduchon-Truchot in a *Contribution to the Study of the Kjeldahl Process Employing Perchloric Acid.*[9] The boiling solution of concentrated sulphuric acid, and the decomposition products of the organic material, were treated dropwise by the addition of perchloric acid avoiding excess beyond the minimum required to finally decolorize the reaction mixture. By such procedure the determination of amino-nitrogen in the wet ashed solution was successfully applied.

This procedure was again investigated by M. Oosting[8] as a wet ashing process. The organic composition was heated in contact with concentrated sulphuric acid and then oxidized by the dropwise addition of perchloric acid. Added perchloric acid was left in contact with the organic matter until consumed before additional dropwise addition of oxidant. Chromium as potassium dichromate, vanadium as ammonium vanadate and selenium dioxide in 5-mg amounts were used as catalysts. Vanadium was found to be the most effective of the three.

No reference has been found in which the use of sulphuric-perchloric acid mixtures were employed in wet ashing processes at controlled and graded high oxidation potentials.

THE OXIDATION OF DARCO DECOLORIZING CARBON AND COCONUT CHARCOAL

A sample of 1 g of coconut charcoal (2-3-mm particle size) was placed in a 125-ml Bethge apparatus flask and 4 to 5 mg of ammonium vanadate added. Fifteen ml of a mixture of equal parts by volume of 96.3% sulphuric acid and 69.6% perchloric acid was employed as oxidant. The reflux air- and water-cooled condenser parts of the digestion apparatus were set in place and the heat applied. At 4 minutes the reaction temperature was 209° and the reaction mixture still orange in colour due to the pervanadic acid formed. The particles of carbon were not being oxidized at this temperature. At 5 minutes and 213° the carbon particles began to disintegrate and the solution resulting began to oxidize as indicated by the reduction of the pervanadic acid and the black colour of the reacting solution. At 12 minutes the reaction mixture was yellow in tint and at 15 minutes the reaction was complete and the colour orange due to reoxidized vanadium, indicating the complete destruction of organic matter. There was no acid insoluble residue.

The same reaction conditions in the oxidation of Darco decolorizing carbon (Atlas Powder Co., in one-gram samples) required only 9 minutes digestion for complete oxidation. The Darco oxidation was accompanied by 30 to 35 mm of foam formation and the oxidation was productive of considerable white fumes emitted by the water condenser. The foam quickly subsided and no insoluble matter was evident in the cold, diluted, wet ash residue.

THE WET OXIDATION OF COAL, ANTHRACITE, OR BITUMINOUS, OF HIGH AND LOW VOLATILE COMBUSTIBLE MATTER

The determination of arsenic in coal has formerly been carried out following wet oxidation using mixed nitric and sulphuric acids. This procedure is time-consuming, and is complicated by troublesome foam production. The presence of complex heterocyclic ring nitrogen compounds requires a more effective oxidant. The wet oxidation of coal employing mixed perchloric and sulphuric acids overcomes these three limitations.

For such wet oxidation of coal a two-stage reaction is involved. First the volatile combustible matter (the V.C.M. of the proximate analysis of coal) is oxidized. The required oxidation potential is not excessive for this stage of the reaction. The second stage of the oxidation demands a much higher oxidation potential. Foam formation accompanies the first stage but not the second stage. The first stage is markedly exothermic and must be temperature controlled. The second stage is carried out at higher temperature and vanadium is added as catalyst.

The procedure found best suited for the wet oxidation of coal is as follows:

The Bethge digestion reaction with 125-ml reaction flask is suited to the oxidation of one gram samples.

The first stage reaction employs 2.5 ml of 96.3% sulphuric acid and 7.5 ml of 69.6% perchloric acid. No vanadium catalyst is present.

The gas flame is lit and in less than 2 minutes the temperature is 80 to 85°. At this point the heat is cut off by closing the screw-clamp of the gas supply tube, and the exothermic reaction resulting carries the reaction temperature to 180 to 185°. The foam formation at this stage is from a small amount, approximately 15 mm for anthracite coal, to 50 mm for bituminous high V.C.M. type coal. After a 5-minute time interval for reaction the temperature begins to drop slowly. A 5-ml portion of sulphuric acid in which 5 to 6 mg of ammonium vanadate is dissolved, is then added through the water-condenser and the heat again applied. The completion of the digestion follows in 15 to 20 minutes for anthracite, 13 to 14 minutes for Pocahontas coal, and 9 to 10 minutes with high volatile Orient (Southern Illinois) coal.

A feature of the wet oxidation reaction with equal parts by volume of sulphuric and perchloric acids (effective perchloric acid concentration 100%) is the formation of decomposition products which during the early stage of oxidation issue as white fumes out of the top of the water-condenser. These are due to the dissociation of 100% perchloric acid into chlorine, oxides of chlorine and oxygen. No indication of an oily reflux of decomposition products from the coal is noted by examination of the inside walls of the air-condenser. This indicates no loss of volatile combustible matter through the water-condenser.

WET OXIDATION OF COAL AS A SINGLE STAGE REACTION

The oxidation of coal may be applied as a single-stage reaction. The mixed sulphuric and perchloric acids, of the same strength and proportions previously described, with added vanadium catalyst, serve to oxidize 2 g of Orient high V.C.M. coal using a 500-ml reaction flask.

The temperature after 2 minutes heating was 66°. White fumes filled the reaction flask. After three minutes the temperature was 110° and rapidly increasing. At 4 minutes the temperature was 225° and there was 50 mm of foam over the boiling reaction acids. At 5 minutes the foam had subsided and the reacting acids turned the colours black to red-brown; the temperature had fallen to 202°. At 8 minutes the temperature was 203° and the reaction mixture yellow in colour. With the reflux return cut off the temperature increased to 210° at the 14-minute interval and the oxidation was complete.

The fumes escaping from the water-condenser in this reaction were collected in a cold trap immersed in a dry ice-acetone bath. There were thus collected 2.35 g of condensate. There remained a yellow oil, weight 1.05 g, after warming to room temperature. This constituted the unoxidized volatile combustible matter from the coal oxidation. The reflux collected in the air-condenser had a volume of approximately 3.0 ml.

Essentially the same results were attained with 12.5 ml of sulphuric acid plus 15 ml of perchloric acid in the oxidation of 2 grams of the same coal. In this case the exothermic reaction carried the temperature to 202° in 7 minutes. At this point the reflux return was cut off and the reaction complete after 30 minutes with other results the same.

A 3-g sample of anthracite coal was similarly oxidized using 18 ml of sulphuric acid and 15 ml of perchloric acid again with 2-3 mg of vanadium as catalyst. In this case there was no appreciable foam formation. The exothermic reaction carried the temperature to 208° at the 8-minute interval. The return of reflux was cut off at 25 minutes and the reaction complete at 50 minutes. The cold trap condensate was 2.35 g reduced to approximately one gram at room temperature, with high volatile matter being lost.

Under the same conditions a 2 g sample of Pocahontas coal gave the same type results except that the starting acid mixture was 10 ml of sulphuric acid and 15 ml of perchloric acid. The reaction produced 15 mm of foam at the 5 minute interval at 224°, indicating again a markedly high exothermic reaction. At 13 minutes the reflux return was cut off and the reaction complete in 30 minutes. The reflux collected in the air condenser had a volume of 4.5 ml. The cold trap condensate again was approximately 1 ml at room temperature.

The determination of arsenic in coal following procedures as described presents the problem of the possible loss of arsenic by either volatilization or retention in the acid insoluble ash.

These same problems exist in a wet oxidation procedure which employs mixed nitric-sulphuric acid as reactants. By reasonable prediction, no arsenic will be lost by volatilization in wet ashing because of the high potential provided to maintain the arsenic in its higher valence state.

Loss by retention of arsenic by the ash residue must be proven following either wet or dry preliminary ashing procedures.

PRE-DIGESTION BY SULPHURIC ACID FOLLOWED BY FINAL OXIDATION WITH ADDED PERCHLORIC ACID

As previously shown, carbon as coconut charcoal or Darco decolorizing carbon, may be wet ashed employing boiling mixed sulphuric and perchloric acids with added vanadium catalyst. With the two concentrated acids, and equal volume mixtures, an effective perchloric acid of 100% strength is provided.

This suggests a preliminary digestion with concentrated sulphuric acid. The carbonization of the sample having been accomplished, the subsequent addition of perchloric acid rapidly completes the oxidation. Such a procedure is more time consuming but has the advantage that foam formation is avoided.

The wet oxidation of ion-exchange resin IR–120 was employed to demonstrate this type reaction.

The Bethge digestion apparatus with 500 ml reaction flask was charged by the addition of 2 grams of sample, 2 to 3 mg of vanadium and 15 ml of concentrated sulphuric acid. A 60-minute digestion period was employed for this reaction (at 15 minutes 180°, at 30 minutes 185° and at 60 minutes 220°). The inner side walls of the reaction flask at this point were well spattered with charred sample reactants and the solution well charred and jet black.

At this point there was added (by pouring through the water condenser) 5 ml of 70% perchloric acid.

In 2 to 3 minutes the temperature rose to 230° and receded to 210°. The side walls of the reaction flask were completely clear of black deposit. The reaction of oxidation was complete in 10 minutes of the second stage at a temperature of 203°. The cooled acid residue was turbid but dilution with an equal volume of water gave a clear solution.

This procedure was applied with equally good results to dried whole milk powder. It constitutes a general method of attack.

THE WET ASHING OF WOOL AT HIGH OXIDATION POTENTIAL

This reaction may be carried out by any one of three procedures.

1. By use of mixed nitric plus perchloric acid,[3] with and without vanadium as catalyst.
2. By reaction with 64.5% boiling perchloric acid,[3] with vanadium as catalyst.
3. By digestion with equal volumes of 96.3% sulphuric and 69.6% perchloric acid in the presence of vanadium for catalysis. Reaction 3 is the most rapid. It was demonstrated as follows:

The Bethge apparatus (250 ml flask) was charged with 1 g of wool yarn, 2 to 3 mg of vanadium and 15 ml of equal parts by volume of concentrated sulphuric acid and 69.6% perchloric acid.

The digestion was at low heat. At 2.5 minutes the sample was completely in solution (dark brown) and at 90°. At 3 minutes it was at 122° with brisk ebullition. At 3.5 minutes the temperature was 165° with foam formation of 10 mm. At 4 minutes the temperature was 200°C with 25 mm of foam formation and the colour changed from brown to green. At 4.5 minutes and 205° the foam subsided. At 5 minutes the temperature was the same and the reacting solution yellow. The reaction was complete in 6 minutes at 203° and orange in colour from pervanadic acid which indicates complete oxidation. The cool reaction mixture deposited crystals of ammonium perchlorate but gave a clear solution after dilution.

THE WET OXIDATION OF THE MOST OXIDATION-STABLE ORGANIC MATERIALS

The wet oxidation of quinoline serves as an example. A 2-ml sample (2.2 grams) was digested in the Bethge apparatus using a 250-ml flask. The oxidant was 15 ml of equal parts by volume of concentrated sulphuric acid and 96.6% perchloric acid with 2 mg of vanadium as catalyst (effective perchloric acid strength 100%).

With 4 minutes heating the temperature was 190° and vigorous reaction set in. The temperature after 5 minutes was 214° accompanied by the formation of 25 mm of foam. At 6 minutes the temperature was 225° and the solution changed from dark-brown to red-brown. At 8 minutes the temperature fell to 218° and the reactants were yellow in colour with no foaming. At 10 minutes the temperature was 225° and reaction complete as indicated by the pervanadic acid colour.

The wet ash residue was evaporated to remove excess acid. After removal of perchloric followed by sulphuric acid, there remained, upon cooling, a white crystalline residue soluble in water and strongly acidic in reaction. A sample of this residue was neutralized to pH 5.5 and copper sulphate added. A blue insoluble precipitate was obtained indicating the reaction product to be nicotinic acid.

Such oxidation has been employed for the patented procedure in the manufacture of nicotinic acid.

THE WET OXIDATION OF 8-HYDROXYQUINOLINE

The same reaction oxidant as employed for the oxidation of quinoline was employed. A 1-g sample of "oxine" was wet ashed with complete oxidation in less than 10 minutes digestion. The wet ash was evaporated to remove the mixed acids and the catalyst and a small amount of ammonium sulphate only remained.

The oxidation of both ring structures of "oxine" was in this case complete as distinct from the partial oxidation of quinoline only to nicotinic acid.

A one-gram sample of Snyder's reagent (4:7-dihydroxy-1:10-phenanthroline) was oxidized under the same conditions. The reaction was complete in 10 minutes and the wet ash upon evaporation to remove the excess acids showed only the catalyst as a residue. This oxidation was accompanied by no carbonization by the hot acid medium.

WET OXIDATION OF SYNTHETIC FABRIC MATERIALS

This oxidation is difficult to carry out employing procedures other than high oxidation donors. The mixed acids used were equal parts of 96.3 % sulphuric acid and 69.6 % perchloric acid with 1 to 2 mg of vanadium as catalyst. The Bethge digestion apparatus with 250-ml reaction flask was employed at moderate heat. The results are given in Table I.

Table I. The wet oxidation of nylon, dacron and orlon

Time, *min*	1	1.5	2.0	2.5	3	3.5	4	5	6	7	8
Nylon	54°	–	66	90	123	194	213	213	210*	–	–
Dacron	47°	54	65	80	105	165	209	209	210	211	211*
Orlon	41°	150	192	218	218	215	214	214*	–	–	–

* Oxidation complete.

All three materials were exothermic in reaction to a marked degree. No carbonization degradation products were formed. Foam formation was pronounced with Nylon and Orlon, but normal with Dacron. The residual acid solution of the ash was clear in each case when hot. When cool a precipitate of ammonium perchlorate formed in the case of Nylon and Orlon but not with Dacron. Upon dilution with water, all gave clear solutions except Orlon. With Orlon the oxidation was most rapid and the exothermic nature of the reaction the most pronounced.

THE WET ASHING OF RUBBER

The procedures previously employed were digestion with mixed nitric and perchloric acids. Their general adoption for routine analytical control has been retarded, due to fear of attending uncontrolled reaction rates.

For analyses, other than the determination of sulphur, predigesting with hot concentrated sulphuric acid is a recommended procedure.

A 1-gram sample of pure gum rubber, finely divided, was placed in a 250-ml Bethge apparatus flask. Concentrated sulphuric acid (7.5 ml) was added and 1 to 2 mg of vanadium. The pre-digestion period was 10 minutes at 200°. The inside walls of the flask were coated black from spray reaction products, the solution was carbonized and black, and sulphur dioxide escaped from the water-condenser.

The reaction mixture was cooled to 40° and 7.5 ml of 69.6 % perchloric acid added by pouring through the water-condenser. Heating for 3 minutes imparted 100° to the reaction and oxidation was initiated with the formation of 50 mm of foam. At 5 minutes the reaction temperature was 200° and oxidation vigorous. At 8 minutes the solution was dark brown and at 215°. In the reaction period 8 to 20 minutes the temperature fell to 188°, the solution changed from brown, through red, then yellow, and finally to orange, to indicate completion of oxidation.

The wet ash was clear when hot, turbid when cold and clear again with dilution.

PROCEDURAL GENERALIZATIONS

By the application of one of the three general methods above cited in the oxidation of wool, practically any sample of organic composition may be successfully and rapidly wet ashed.

For recovery of sulphur in the wet ash residue, nitric acid must be one portion of the oxidizing acid mixture. Boiling 72.5% perchloric acid fails to retain sulphur quantitatively as sulphuric acid. Small portions, in the absence of nitric acid, are converted to sulphuryl chloride and evolved. Procedures (2) and (3) retain arsenic, phosphorus and metallic major and minor constituents quantitatively. Following reaction types (1) and (2) silica may be determined. This procedure requires evolution of nitric acid, if involved, dilution and filtration.

For the determination of arsenic, phosphorus and molybdenum there are available spectrophotometric procedures of high sensitivity. For the determination of Fe, Cu, and Co, the procedures may employ the chromophore group specifics, (=N—C—N=) such as 1:10-phenanthroline or its many derivatives. These include "cuproïne," "neocuproïne," "bathophenanthroline," "bathocuproïne," "Snyder's reagent," "Terosite," terpyridine and bipyridine among other examples.

By all these processes the sensitivity is such that it is seldom necessary to wet ash samples larger than one gram.

The Bethge apparatus for digestion provides a ready means of removal of excess acid, with retention of the distillate. This provides for retention of any evolved elements for determination if loss by volatility is suspected.

There is available a wide range of oxidation potentials from moderate to the highest attainable. Static control of specific oxidation potentials is assured. The elimination of all hazard from uncontrolled reaction rates is assured. The study of reaction conditions resulting in the least requisite time may be made, employing a wide variety of acid mixtures, reagent concentrations and proportions including temperature control. All these variables create flexibility which cannot be duplicated, even remotely, by the use of oxidation media in the absence of perchloric acid.

Boiling 72.5 per cent perchloric acid alone cannot be employed to oxidize cellulose, sugars, or alcohols or compositions rich in these ingredients. Violent reactions are certain to result. By the simple expedient of oxidation with mixtures of nitric acid and perchloric acid combined, such oxidations are entirely practical and a very large number of routine control analyses without the least hazard are in constant routine application.

Boiling diluted perchloric acid (55% to 65%) concentration maintained by use of the Bethge apparatus through reflux return, is admirably adapted for the wet oxidation of products rich in cellulose, proteins and sugars.[3]

For organic compositions requiring the highest oxidation potential such as coal, ion-exchange resins, alkaloids, carbon and heterocyclic ring nitrogen structures such as caffein, the use of mixed sulphuric and perchloric acids represents a very important series of reactions. The use of vanadium as catalyst serves to temper and shorten oxidation periods. The presence of sulphuric acid serves the same dual purpose.

In establishing correct procedures for any new type wet oxidation no hazard is involved. A 10-milligram sample may be first tested. If the particular reaction composition gives a controlled oxidation it may be increased to 100 mg, then to 500 mg and finally to 1 gram samples or larger. The use of an operator's protective scheme, such as a transparent reaction flask shield is not an admission of possible ensuing violent reaction, but is rather a sensible protection. This is a correct procedure with many reactions in which perchloric acid has no part.

Perchloric acid is, without fear of refutation, the most versatile analytical reagent known. Study of its basic chemistry and familiarity with its multiplicity of applications receives far too little study. Its use contributes speed, accuracy, and convenience for hundreds of analytical operations. It is a fault to outlaw its use as a result of misinformation. One thus avoids the real labour of experimentation. Wet oxidations are indeed but a small part of the rich rewards of its multiplicity of reaction advantages.

FURTHER APPLICATIONS

Many specific applications in wet oxidation procedures besides those described have been omitted from this account although successfully applied. By the use of the apparatus described, and by following the considerably varied processes experimentally demonstrated herein, few if any situations defy successful methods of attack.

For a general review of the role of perchloric acid in procedures of wet oxidation consult H. Diehl and G. Frederick Smith.[10]

Zusammenfassung—Es wurde eine Untersuchung von oxydative Kraft (Potential) der Überchlorsäure und Schwefelsäure-Überchlorsäure Mischungen zwecks Zerstörung der organischen Substanzen nasser Veraschung vorgemommen. Das Oxydationspotential wurde an Fe-II bis Fe-III und Cr-III—CrO_3 angewandt geprüft. Die Gegenwart von Schwefelsäure vergrössert das Potential der Überchlorsäure, und stimuliert der Verlauf der Reaktion. Vanad in kleiner Menge (1–2 mg) dient dem gleichen Zwecke, und reguliert auch die Kinetik der Oxydation. Die bearbeitete Technik wurde auf Probe von Kohle, Ionaustaucherharze, Alkaloide und syntetische Stoffe angewandt, und befriedigend gefunden.

Résumé—Le potentiel d'oxydation de l'acide perchlorique à son point d'ébullition est une fonction de la température et de la concentration. A la température ordinaire, on ne peut déterminer aucun potentiel d'oxydation dans le domaine de concentration de 0 à 73,6%. A la température d'ébullition l'acide perchlorique à 50% ne réussit pas à oxyder Fe (II), si ce n'est très lentement. A une acidité de 72,5% (concentration azeotropique), l'acide bouillant (203°C) est un oxydant puissant. Par exemple Cr (III) est facilement oxydé en CrO_3. Pour des concentrations comprises entre 50 et 72,5%, l'acide bouillant a des potentiels d'oxydation continuellement croissants. Par le contrôle de concentrations convenablement choisies au moyen de l'ébullition à reflux, on peut imaginer de nombreuses méthodes pratiques pour des oxydations contrôlées par voie humide de composés organiques.

Pour avoir des potentiels d'oxydation élevés, il faut de fortes concentrations d'acide perchlorique. Par addition d'acide sulfurique concentré en quantités variables en volume à de l'acide perchlorique à 70%, les concentrations effectives de ce dernier peuvent augmenter et atteindre 100%. De nouveau, par le contrôle de concentrations particulières des mélanges d'acides choisis au moyen de l'ébullition à reflux, on peut obtenir des potentiels d'oxydation extrêmement élevés, sous contrôle statique.

L'utilisation d'acide sulfurique dans de telles applications remplit la fonction supplémentaire importante de maitriser la réaction et contrôler les vitesses de réaction. L'addition de 1 à 2 mg de vanadium comme catalyseur de la réaction a le même but. Le vanadium influence aussi favorablement la cinétique de la réaction tout en raccourcissant la période d'oxydation nécessaire.

Des méthodes utilisant cette réaction ont été démontrées ici expérimentalement. L'oxydation par voie humide d'échantillons tels que charbon, résines échangeuses d'ions, alcaloïdes, matériaux synthétiques servent d'exemples. Aucune réaction dangereuse n'a été rencontrée dans ce travail.

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THE DETECTION OF CARBON IN SPOT TEST ANALYSIS*

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Summary—If organic compounds are dry heated with mercuri-amido chloride or with a mixture of mercuric oxide and ammonium chloride, hydrogen cyanide results. The latter can be sensitively detected through the colour reaction (blue colour) when the gas phase is permitted to come into contact with filter paper moistened with a solution of copper acetate and benzidine acetate. This detection of carbon can be accomplished within the technique of spot test analysis; the limit of identification is 1 μg carbon.

THE problem of detecting carbon or more correctly carbon-containing compounds arises when testing for the presence of metal-organic compounds, or in testing the purity of inorganic materials, and also when studying the evaporation residues of commercial waters. Emich[1] has described a microchemical method for detecting carbon based on the detection of carbon dioxide produced by burning the sample, but in addition to requiring delicate apparatus and exact handling, this method has the further disadvantage of not being applicable when carbonates are also present. Feigl and Goldstein[2] have described procedures for spot test purposes, which make use of sensitive redox reactions and which are not impaired by carbonates. However, oxidizing or reducing inorganic compounds do interfere and hence these must be completely removed before applying the test.

For these reasons, special interest resides in a procedure proposed by Mamose[3] and his associates, which though impaired by carbonates, which are readily removed, is not subject to interference by inorganic compounds that have oxidising or reducing properties. This test is based on the formation of sodium cyanide when organic compounds and inorganic compounds containing carbon are dry-heated with sodium amide (m.p. around 200°). Wöhler[4] found that sodium amide decomposes into its elements when heated and that sodium cyanide results on heating with carbon. Accordingly, the Mamose procedure probably involves the simultaneous production of free sodium, carbon and nitrogen, and also the marked combining power of the latter two elements. This view is supported by the finding of Mueller[5] that sodium cyanide results if organic compounds are heated with sodium azide, which itself decomposes when heated and gives sodium and nitrogen. Since very sensitive tests are available for cyanides, it could confidently be expected that sensitive tests for carbon might be developed on the basis of pyrolysis of the sample in the presence of sodium amide or sodium azide.

However, trials showed that, within the technique of spot test analysis, the formation of sodium cyanide by dry heating of organic compounds with sodium amide or azide occasionally fails completely or takes place to an unsatisfactory extent. Moreover, the explosive decomposition in the presence of sodium azide is a handicap. The reason for the failure was to be sought in an effect, which Feigl[6] has termed

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pyrohydrolysis, and which he has employed in qualitative organic analysis. Pyrohydrolysis involves fundamentally the action of water that is released as quasi-superheated steam during the dry heating of metal salt hydrates or organic compounds; such steam is capable of bringing about reactions that by the wet method are not realizable at all, or not to more than a minor extent. Accordingly, when the organic compounds give off water when dry-heated in the vicinity of the melting- or decomposition-temperature of admixed sodium amide or sodium azide, the following hydrolysis occur:

$$NaNH_2 + H_2O \longrightarrow NaOH + NH_3$$

$$NaN_3 + H_2O \longrightarrow NaOH + HN_3$$

Since these hydrolyses destroy the sodium amide or azide, the formation of cyanide during the pyrolysis steadily decreases and finally ceases. Hence the yield of cyanide will be insufficient in many cases to provide a satisfactory test.

It has now been found that a reliable production of cyanide can be achieved, without impairment by pyrohydrolysis, if the organic sample is dry-heated in the presence of mercuri-amido chloride, commonly known as infusible white precipitate. When the sample is heated in the presence of this compound hydrogen cyanide gas is formed, which can be readily detected in the gas phase by the well known and widely-used colour reaction of Sievert and Hermsdorf.[7] No experimentally substantiated statements can be made regarding the reaction path leading to hydrogen cyanide. However, the net reaction can be written:

$$HgNH_2Cl + C \longrightarrow Hg + HCl + HCN$$

The procedure given here has the following advantages. The method is applicable to all organic compounds; if certain precautions are taken, even volatile samples can be successfully tested. Organic compounds containing sulphur, which according to Mamose decrease the yield of sodium cyanide because of the formation of thiocyanate, do not interfere. Obviously the sulphur is fixed and immobilized as mercury sulphide. No pyrohydrolysis occurs. In contrast to sodium amide and sodium azide, the mercuri-amido chloride is neither hygroscopic nor does it explode on heating. A mixture of mercuric oxide and ammonium chloride may be substituted for the complex mercuric chloride.

Procedure: Conduct the test in a micro test tube fixed in an asbestos board support. Add a small amount of the solid or liquid material to be tested or a drop of its solution to a few cg of mercuri-amido chloride or a 1 : 5 mixture of mercuric oxide and ammonium chloride. Cover the mouth of the test tube with a disc of filter paper moistened with the reagent solution. Begin heating at the upper end of the test tube and proceed downward. A blue stain appears on the paper if the response is positive.

Reagent solution: Equal volumes of (*a*) and (*b*) are mixed before the use.

(*a*) 2.86 g of copper acetate in a litre of water.

(*b*) 675 ml of a solution of benzidine acetate, saturated at room temperature, and 525 ml water.

About fifty organic compounds of different types were examined and the limit of identification of 1 μg carbon was obtained. Only urea fails to give a satisfactory sensitivity.

The test as described here has been proved effective for detecting organic materials in the evaporation residues of water samples. Tests directed towards the detection of organic dust particles are in progress.

Acknowledgement—The authors are indebted to Professor Fritz Feigl for valuable counsel in the course of these studies.

Zusammenfassung—Wenn organische Verbindungen im trocknen Zustande mit Merkuriamidochlorid oder mit einer Mischung von Merkurioxyd und Ammoniumchlorid erhitzt werden, entsteht Cyanwasserstoff. Dieser kann sehr empfindlich über die blaue Farbe, die aus der Reaktion zwischen mit Kupferacetat und Benzidinacetat angefeuchtetem Filtrierpapier und der Gasphase eintritt, bestimmt werden. Dieser Tüpfelnachweis auf Kohlenstoff weist eine Erfassungsgrenze von 1 μg Kohlenstoff auf.

Résumé—Si on chauffe à sec des composés organiques avec du chloro-amidure de mercure ou avec un mélange d'oxyde mercurique et de chlorure d'ammonium, il se forme de l'acide cyanhydrique. On peut déceler ce dernier de manière sensible au moyen d'une réaction colorée (couleur bleue): on met en contact la phase gazeuse avec un papier filtre imprégné d'une solution d'acétate de cuivre et d'acétate de benzidine. On peut faire cette recherche du carbone par la méthode d'analyse à la touche. La limite d'identification est 1 μg de carbone.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH THIOMALIC ACID

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Summary—A procedure has been developed for the ultraviolet spectrophotometric determination of palladium^{II} with thiomalic acid. Maximum absorbance of the yellow organo-palladium complex, PdR_2, is at 350 mμ; the optimum pH range is 1.1 to 2.6.

The colour reaction is instantaneous and the complex is stable for several days. Temperature variation over the range 15° to 35° has no significant effect. The coloured complex obeys Beer's law and the practical sensitivity of the reaction is 0.05 ppm of palladium.

Tolerances to a number of ions have been established and palladium has been determined in a variety of synthetic samples with good precision and accuracy.

SEVERAL reagents have been reported for the spectrophotometric determination of palladium. The most sensitive of these are *p*-nitrosodiphenylamine, *p*-nitrosodimethylaniline and *p*-nitrosodiethylaniline proposed by Yoe and Overholser.[6,10] Later work by Cheng,[1] using 2-nitroso-1-naphthol, provided a relatively simple method which is free from most of the usual interference. His method is somewhat simpler and freer from interferences than the method of Yoe and Overholser; however, it requires the extraction of the palladium complex into toluene. A method which can be carried out in aqueous media and which is rapid, sensitive and relatively free from interferences is desirable. It is the purpose of this paper to present such a method.

APPARATUS AND REAGENTS

Instruments

Absorbance measurements were made either with a Beckman ratio recording spectrophotometer, Model DK-2, using matched 1.00-cm quartz cells or with a Beckman spectrophotometer, Model DU, using matched 1.00-cm Corex cells.

All pH measurements were made with a Beckman glass electrode pH meter, Model G.

Reagents

Thiomalic acid: The thiomalic acid (mercaptosuccinic acid) was obtained from the National Aniline Division, Allied Chemical and Dye Corporation, Buffalo, N.Y. Results of analysis showed $C = 31.95\%$, $H = 4.15\%$; calculated, $C = 32.0\%$, $H = 4.03\%$ based on the formula $HOOCCH_2CH(SH)COOH$. The compound is colourless and highly soluble in water. Its melting range is 150° to 152° and its ionization constant is 5.2×10^{-4} at 20°. Aqueous solutions of thiomalic acid (henceforth abbreviated TMA) are slightly unstable. For this reason, fresh solutions in distilled water were prepared daily or when needed. This was entirely satisfactory because there is no effect on the colour reaction when the reagent solution is less than twenty-four hours old. Solutions used in this investigation were 0.01 molar.

Standard palladium solution: Eighty-five millilitres of concentrated hydrochloric acid was used to dissolve 1.74 grams of palladous chloride and distilled water was added to give a final volume of

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one litre. This gave a solution one molar in hydrochloric acid and containing approximately 1000 ppm of palladium. Standardization was carried out gravimetrically by the dimethylglyoxime method.[3] Triplicate analyses in good agreement gave an average value of 1054 ppm of palladium. A solution containing 100 ppm was prepared by taking an aliquot of the standard solution and diluting to the proper volume.

Buffer: A Clark and Lubs buffer of pH 2.0 was prepared by mixing 53 ml of 0.2*N* hydrochloric acid and 250 ml of 0.2*N* potassium chloride, and diluting to one litre.

Solutions of diverse ions: Reagent-grade salts were used to prepare solutions of the various ions; stock solutions generally contained 1 mg of the ion per millilitre of solution.

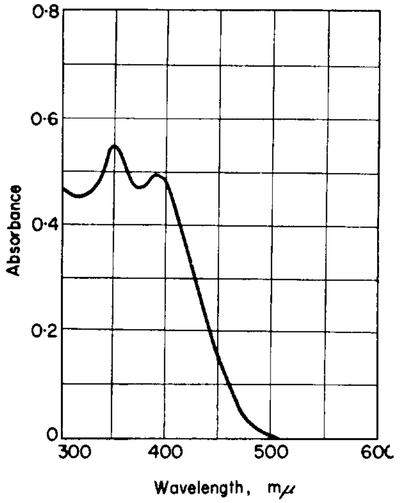

FIG. 1. Absorbance curve of the palladium complex with thiomalic acid.

EXPERIMENTAL AND DISCUSSION

When a drop of a 0.5% solution of TMA is added to a drop of palladium^{II} solution (0.05 mg Pd) on a spot plate, a bright yellow colour is formed at once. This reaction was reported in 1948 by König and Crowell.[5]

The absorbance spectrum for the yellow organo-palladium complex is shown in Figure 1. The absorbance maximum is at 350 mμ; the reagent does not absorb at wavelengths above 290 mμ and a water "blank" is satisfactory.

Effect of pH

The complex is formed at all pH's; however, maximum absorbance is obtained over the pH range 1.1 to 2.6. Ten millilitres of a Clark and Lubs buffer of pH 2.0 in a total volume of 25 ml is sufficient to maintain the pH well within the useful range.

Concentration of reagent

An excess of TMA is desirable since the absorbance of the complex is increased somewhat with increasing concentration of reagent. An excess of reagent also increases the tolerances to several diverse ions. Five millilitres of a 0.01*M* TMA solution was found satisfactory for a total volume of 25 ml.

Order of addition of reagents

The order of addition of the acid solution containing palladium, the TMA, and the buffer is not critical. If the absorbance is to be measured immediately, however, the buffer must be added last. An hour is required for the colour reaction to reach maximum absorbance if the buffer is added first or second. The absorbance remains constant for at least three days.

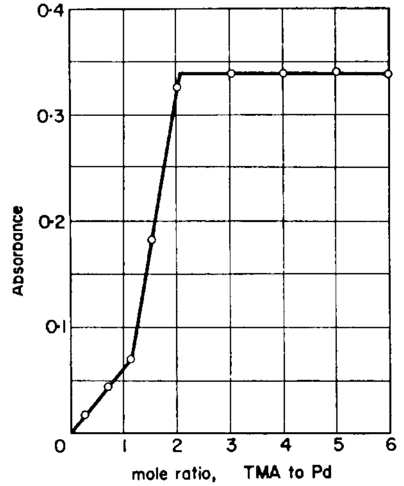

FIG. 2. Mole ratio of the palladium complex with thiomalic acid; palladium concentration constant, reagent concentration varied.

Temperature

Temperatures over the range 15° to 35° have no significant effect on the palladium complex.

Beer's law

Beer's law is obeyed over the concentration range 0.4 to 10 ppm of palladium, the most sensitive range being 2 to 7 ppm which give absorbances of 0.198 to 0.676.

Structure of the palladium complex

Three methods were employed to establish the mole ratio of the complex in solution: (1) the mole ratio method of Yoe and Jones,[9] (2) the continuous variations method of Job[4] as modified by Vosburgh and Cooper,[8] and (3) the slope ratio method of Harvey and Manning.[2] Results of the three methods show a stable complex consisting of two molecules of TMA to one palladous ion. There is also a less stable one-to-one complex formed which does not absorb as strongly as does the two-to-one complex. (Figures 2, 3, 4.)

The following organic liquids were used in an attempt to extract the palladium complex from an aqueous solution (pH = 2.18): chloroform, ethyl acetate, diethyl ether, iso-amyl alcohol, cyclohexanol, *o*-dichlorobenzene. None of the liquids extracted the yellow complex to a visible extent, a strong indication that the complex is ionic in aqueous solution.

Procedure

The sample weight should be chosen so that a convenient volume will contain 50 to 175 ppm of palladium. Thus, a 1-ml aliquot of this solution, diluted to 25 ml, will contain 2 to 7 ppm of palladium.

Dissolve the sample by any appropriate method. Adjust the solution to the proper concentration and transfer a 1-ml aliquot by means of a pipette to a 25-ml volumetric flask. Add 5 ml of a freshly prepared 0.01*M* TMA solution and 10 ml of a hydrochloric acid-potassium chloride buffer of pH 2.0. Dilute the solution to the mark and thoroughly mix. Then measure the absorbance at 350 mμ and read the palladium concentration from a calibration curve prepared by the same procedure.

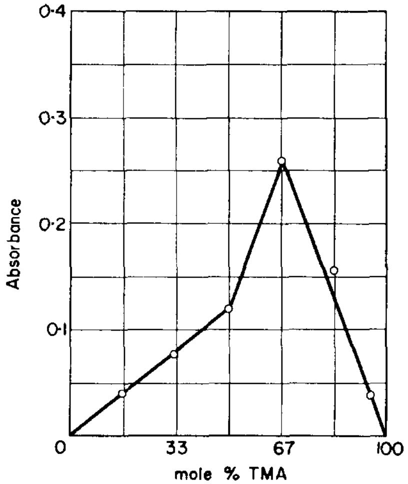

FIG. 3. Continuous variations of the palladium complex with thiomalic acid Curve (1), reagent in large excess; Curve (2), palladium in large excess.

Note: The first slope in Curve (2) is due to the formation of a 1 : 1 complex which absorbs less than the 2 : 1 complex. The second slope in Curve (2) was used to establish the 2 : 1 ratio.

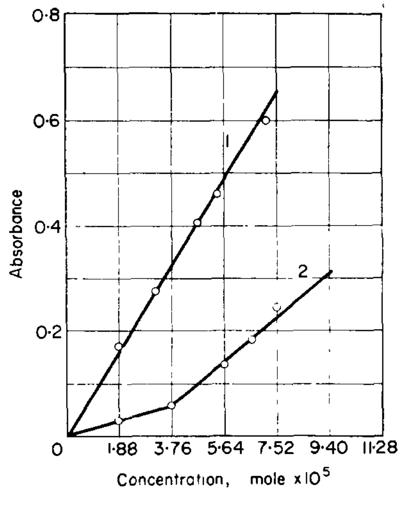

FIG. 4. Slope ratio of the palladium complex with thiomalic acid.

Sensitivity

According to the Beer's law curve for the palladium complex, a concentration of 0.05 ppm of palladium should give an absorbance of 0.005 unit. Absorbance measurements of six solutions, each containing 0.05 ppm of palladium, gave values of 0.005, 0.006, 0.005, 0.005, 0.006, 0.005. Thus, 0.05 ppm of palladium may be taken as the practical sensitivity of the method. The sensitivity according to Sandell[7] is 0.010 μg Pd/cm^2.

TABLE I. TOLERANCE TO DIVERSE IONS

(4.00 ppm Pd)

Ion	Added as	Limiting concentrations *ppm*
Platinum$^{\mathrm{IV}}$	H_2PtCl_6	15
Rhodium$^{\mathrm{III}}$	$RhCl_3$	4
Ruthenium$^{\mathrm{III}}$	$RuCl_3$	3
Osmium$^{\mathrm{VI}}$	K_2OsO_4	3
Iridium$^{\mathrm{IV}}$	$IrCl_4$	20
Gold$^{\mathrm{III}}$	$AuCl_3$	1
Nickel$^{\mathrm{II}}$	$Ni(NO_3)_2$	>100
Cobalt$^{\mathrm{II}}$	$Co(NO_3)_2$	>100
Copper$^{\mathrm{II}}$	$Cu(NO_3)_2$	0.6
Chromium$^{\mathrm{III}}$	$Cr(NO_3)_3$	40
Iron$^{\mathrm{III}}$	$Fe(NO_3)_3$	0.3
Vanadium$^{\mathrm{IV}}$	$VOCl_2$	80
Sulphate	Na_2SO_4	>10,000
Nitrate	KNO_3	>10,000

Tolerance to diverse ions

A concentration of 4.00 ppm of palladium was used in this study. An ion was considered to interfere if the resulting solution differed by 0.005 absorbance unit from that containing palladium alone, *i.e.*, 0.388 ± 0.005.

Table I lists the tolerances to the metals commonly found with palladium.

Analysis of synthetic solutions

The results of analyses of synthetic solutions are summarized in Table II. All samples were run in duplicate or triplicate. The values were in close agreement, the averages being recorded in the table.

Precision

The precision was determined for a solution containing palladium alone (4.00 ppm Pd) and for synthetic solution No. 7 (Table II). In each case, eleven determinations were made. From these data the standard deviation, σ, was calculated from the formula $\sigma = \sqrt{\frac{\Sigma d^2}{n-1}}$, where d is the deviation from the mean and n is the number of determinations. The results are given below:

(1) 4.00 ppm Pd only: $\sigma = 0.019$ ppm, *i.e.*, 0.48%.
(2) Synthetic soln. No. 7: $\sigma = 0.022$ ppm, *i.e.*, 0.52%.

TABLE II. ANALYSIS OF SYNTHETIC SOLUTIONS

Series A

No.	Pd Present *ppm*	Other Ions Present, *ppm*							Pd Found *ppm*
		$\mathrm{Pt^{IV}}$	$\mathrm{Ni^{II}}$	$\mathrm{Co^{II}}$	$\mathrm{V^{IV}}$	$\mathrm{Cr^{III}}$	$\mathrm{Fe^{III}}$	$\mathrm{Cu^{II}}$	
1	4.2	8	24	—	4	—	—	—	4.3
2	4.2	—	12	12	—	4	0.2	0.2	4.2
3	4.2	15	100	—	16	—	—	—	4.3
4	4.2	—	100	100	—	40	0.3	0.6	4.2

Series B

		$\mathrm{Pt^{IV}}$	$\mathrm{Rh^{III}}$	$\mathrm{Ru^{III}}$	$\mathrm{Os^{VI}}$	$\mathrm{Ir^{IV}}$	$\mathrm{Au^{III}}$	
5	4.2	4	4	1.6	1.6	4	0.5	4.5
6	4.2	15	2	3	3	5	2	4.6
7	4.2	4	1	1	1	1	1	4.2
8	4.2	8	1.5	1.5	1.5	1.5	1	4.4

CONCLUSIONS

Thiomalic acid has several advantages as a reagent for the spectrophotometric determination of palladium: It is colourless and water soluble; no extraction of the metal complex is required; the colour reaction is instantaneous and the complex is stable; the pH for maximum absorbance is easily controlled; it allows a high tolerance for many ions; laboratory fluctuations in temperature have no significant effect on the complex; the method is simple, rapid, and sensitive and its precision and accuracy are good.

Zusammenfassung—Zur spektrophotometrischen Bestimmung von zweiwertigem Palladium wurde der gelbe Komplex mit Thiomalinsäure, PdR_2, der bei 350 mμ sein Absorptionsmaximum aufweist, herangezogen. Der geeignetste pH-Bereich liegt zwischen 1,1 und 2,6. Die Farbreaktion tritt rasch ein und der Komplex bleibt mehrere Tage stabil. Temperaturänderungen innerhalb 15 und 35° haben keinen merklichen Einfluss. Der gefärbte Komplex gehorcht dem Beerschen Gesetz, und die praktische Empfindlichkeit der Reaktion liegt bei 0,05 ppm Palladium.

Résumé—Les auteurs ont développé un procédé pour le dosage par spectrophotométrie dans l'Ultraviolet du palladium (II) par l'acide thiomalique. Le maximum d'absorption du complexe organopalladeux jaune (PdR_2) est à 350 mμ; le domaine de pH le plus favorable est 1,1–2,6.

La réaction colorée est instantanée et le complexe est stable pendant plusieurs jours. Des variations de température dans le domaine 15–35° n'ont pas d'effet important. Le complexe coloré obéit à la loi de Beer et la sensibilité pratique de la réaction est 0,05 ppm de palladium.

On a établi des tolérances pour un certain nombre d'ions et on a dosé le palladium dans plusieurs échantillons synthétiques avec une bonne précision.

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THE DETERMINATION OF CONDUCTIVITIES USING UNCONVENTIONAL ELECTRODE SYSTEMS*

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Summary—An apparatus is described which permits the measurement of conductivities with non-contacting electrodes.

The use of conventional dipping electrode systems in the determination of electrolytic conductivities is accompanied by a number of experimental difficulties many of which are directly associated with the electrodes themselves and which are often classified under the term "polarisation", whilst in concentrated solutions corrosion and fouling problems are all too common. Many attempts have been made to eliminate the use of immersed electrodes, mostly using high frequency alternating current.[1]

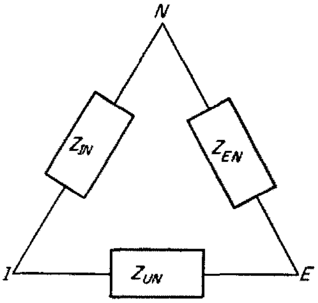

Fig. 1.

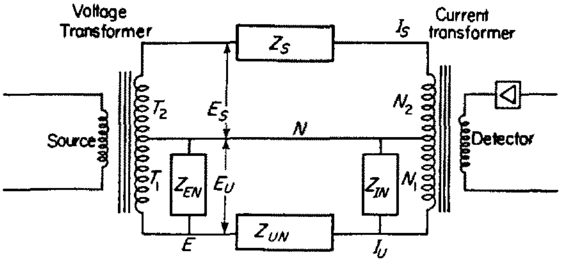

Fig. 2.

The electrode systems described here require the use of a three-terminal transformer ratio-arm bridge.[2,4] The basic circuit of a three-terminal network is shown in Fig. 1, where the impedance to be measured is Z_{UN} but the effects of stray impedances Z_{EN} and Z_{IN} must be removed. Fig. 2 shows the network applied to the bridge. Let E be the voltage terminal, I the current terminal and N the neutral. Assuming ideal transformers, Z_s, the standard impedance is adjusted to give zero voltage at the detector when there must then be zero core flux in the current transformer and

$$N_1 . I_u = N_2 . I_s \tag{1}$$

where N_1 is the number of turns on the windings connected to the unknown, N_2 the number of turns connected to the standard, whilst I_u and I_s are the currents in the unknown and standard.

Under the condition of zero core-flux there is zero voltage across the windings of

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* Presented at a meeting of the Polarographic Society, held at Nobel Division, Imperial Chemical Industries Ltd., Stevenston, Ayrshire, on 26 September 1958.

the current transformer. The connections to both Z_{UN} and Z_s on the current transformer side are thus at neutral potential and hence the voltage across Z_{UN} is E_u and across Z_s is E_s when

$$I_u = E_u/Z_{UN} \tag{2}$$

$$I_s = E_s/Z_s \tag{3}$$

and thus from equation (1)

$$N_1E_u/Z_{UN} = N_2E_s/Z_s. \tag{4}$$

But the voltage ratio, E_u/E_s equals the turns ratio, T_1/T_2, so that at balance the equation becomes:

$$Z_{UN} = \frac{N_1}{N_2} \cdot T_1/T_2 \cdot Z_s. \tag{5}$$

At balance Z_{IN} has no voltage across it and therefore draws no current. Its effect is to reduce the off-balance sensitivity by lowering the detector input impedance. This can be overcome by increasing the gain. The impedance Z_{EN} loads the source, and by drawing current through the source impedance reduces the applied voltage E_u. The measurement, however, does not depend on absolute voltage but on the ratio E_u/E_s. In an ideal transformer this is a constant equal to the turns ratio, and a shunt on one winding reduces the voltages on all windings by the same proportions. Thus, if the transformers are ideal, neither Z_{EN} nor Z_{IN} cause any errors. In practice, whilst the transformers cannot be regarded as ideal and shunt impedances will produce small errors, careful construction can reduce the errors to negligible proportions, and in any case the effects of shunt loading can be compensated.

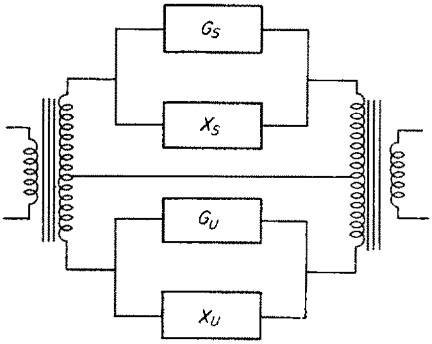

FIG. 3.

Equation (5) can be rewritten in terms of conductances

$$G_u = (G_sT_2) \cdot N_2/T_1N_1. \tag{6}$$

Let (G_sT_2) represent the standard, then it will be seen that it is immaterial whether the number of turns be fixed and the conductance varied, or the conductance fixed and the number of turns varied. Using the latter method the number of standards can easily be reduced to one per decade. In practice the unknown is often a complex impedance, and Fig. 3 shows the bridge such that the standard and unknown impedance have been divided into resistive and reactive components and similar arguments can be advanced for the determination of the reactive component. The measurements are dependent on the product of two turns-ratios and since each of these can easily be 1000 : 1, the overall ratio is a million to one. Further measurement of impedances remote from the bridge presents no great problem since the capacitance of long connecting leads and spurious impedances connected to the measuring terminals are counteracted by the use of the third terminal. The frequency is of little importance and measurements have been made at 100 c/s, 1592 c/s and 10 Kc/s.

Whilst the bridge can be used with conventional electrodes it also permits the determination of conductivity with non-contacting electrodes. Consider the case where T_1 and N_1 are made single turns, so that the balance equation becomes

$$G_u = N_2 . T_2 . G_s \tag{7}$$

The physical nature of the windings is unimportant and there is no reason why the cores of the voltage and current transformers, which in practice are wound on high permeability Mumetal toroidal cores, should not be linked by a closed annulus of conducting liquid contained in an insulating, *e.g.* glass tube. A method of bringing this about is shown in Fig. 4, where an annular glass loop cell is used. The transformers are moulded into an insulating material, and where the electrolyte is inert with respect to the moulding, the probe may be immersed directly in the test-solution, provided the container is large in comparison with the probe. These types of units have been used to determine the conductivity of a variety of solutions, being especially suited to concentrated solutions. The electrolytes used have varied from potassium ferro- and ferricyanides through barium chloride to the conventional uni-univalent electrolytes *e.g.* hydrochloric acid, potassium bromide etc.

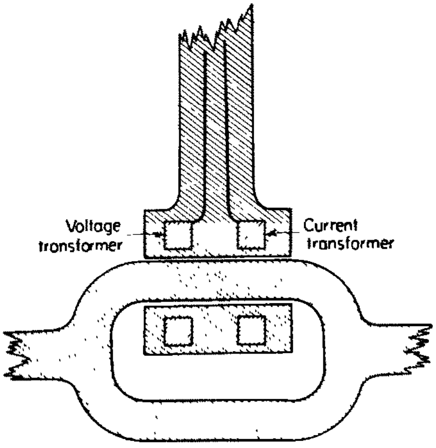

FIG. 4.

The ease with which the bridge determines the capacitance term enables it to be used as a "dielectric bridge." This has allowed the frequent use of the method to determine impurities, such as water, in organic liquids. For this purpose the "capacity cell" shown in Fig. 5 was used. It is necessary to use the "conversion formulae"

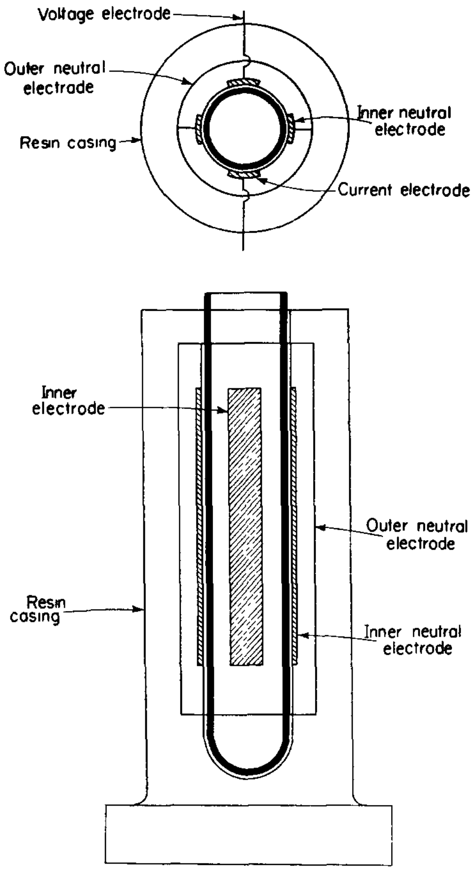

FIG. 5.

shown below where the parallel readings made with the bridge were converted to series readings, due allowance being made for the glass dielectric.

$$C_{ms} = C_{mp} + \frac{G^2{}_{mp}}{w^2 C_{mp}} \tag{8}$$

$$\frac{1}{C_{cs}} = \frac{1}{C_{ms}} - \frac{1}{C_g} \tag{9}$$

where C_g = capacity of glass dielectric
C_{ms} = capacity of "measured series"
C_{mp} = capacity of "measured parallel"
C_{cs} = capacity of "corrected series"
G_{mp} = conductivity "measured parallel"
w = frequency in radians/sec.

Up to 5 % water the results agree well with those of Akerlof and Short,[3] but above this concentration the dielectric constant value obtained is meaningless owing to the effect of relatively small amounts of water (0·1 %-3 %) in organic liquids which have, when pure, low dielectric constants. Indeed, good results have been obtained for water-contaminated acetone (E 21) and also it has been possible to estimate acetone in synthetic cyclohexane-acetone mixtures, although with much less accuracy. For many purposes, where the conductivity term is negligible it has been possible to obtain results from a plot of the parallel against concentration of polar contaminant.

Acknowledgement—The author would like to express his grateful thanks to both Mr. R. Calvert and Mr. K. Fletcher of the Wayne-Kerr laboratories; and to Messrs. Wayne-Kerr laboratories for their generous support.

Zusammenfassung—Es wird ein Apparat beschrieben, welcher die Leitfähigkeitsmessung mit nicht berührenden Elektroden gestattet.

Résumé—L'auteur décrit un appareil qui permet la mesure des conductivités avec des électrodes sans contact.

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THE DETERMINATION OF *vic*-DIOXIMES*

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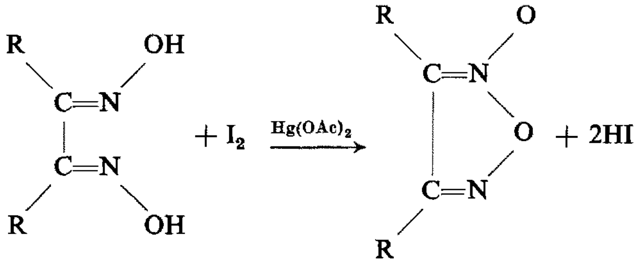
(*Received* 20 *February* 1959)

Summary—Iodine in the presence of mercury^{II} acetate in non-aqueous media quantitatively dehydrogenates *vic*-dioximes to the corresponding furoxanes. This reaction was used to develop a titrimetric method for the quantitative determination of various aliphatic and alicyclic *vic*-dioximes. Fifteen different *vic*-dioximes were titrated successfully by this method. Several of the furoxanes of the *vic*-dioximes were isolated and their physical properties recorded.

INTRODUCTION

THE purity of the *vic*-dioximes is frequently determined by elemental analysis and occasionally by gravimetric precipitation with an excess of nickel.[1,2] The titrimetric methods reported for the determination of nickel using dimethylglyoxime also can be used to assay various *vic*-dioximes. In the titrimetric methods the precipitate of bis(2:3-butanedionedioximato-N:N′)-nickel^{II} is dissolved in acid and the resulting *vic*-dioxime is hydrolyzed to hydroxylamine which is then determined.[3,4] The precipitate also has been dissolved in glacial acetic acid and the resulting acetate groups titrated in a non-aqueous medium.[5] Elemental analysis and any method requiring the filtration of a nickel-*vic*-dioxime precipitate are always time consuming. For this reason a simple and fast oxidation method was devised.

Various chemical reagents have been used for the intramolecular dehydrogenation of *vic*-dioximes. Of the various reagents used—dinitrogen tetroxide,[6,7] sodium hypohalite,[8] alkaline ferricyanide,[6,9] nitrous acid,[10] and chlorine[7]—none possessed suitable characteristics for the development of an analytical method. It was found possible to quantitatively oxidize the *vic*-dioxime group to the furoxane structure using iodine in the presence of mercury^{II} acetate.



(1)

The excess iodine is back-titrated to give the amount of *vic*-dioxime originally present.

Mercury^{II} acetate increases the oxidation potential of iodine solutions because

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[*] No. XXIV in a series on *Chemistry of the vic-Dioximes*. Previous paper in this series is No. XXIII, *Analyt. Chim. Acta*, 1958, **19**, 531.

[†] Contribution No. 723. Work was performed in the Ames Laboratory of U.S. Atomic Energy Commission.

iodide reacts with the mercury^{II} acetate to give slightly dissociated mercury^{II} iodide and mercury^{II} iodide complexes. The oxidation potential increases to such an extent that an "auto-oxidation" of iodine to iodate takes place, removing free iodine from solution. In acid solution, the iodate reacts with iodide to re-form iodine.[11,12]

EXPERIMENTAL

Reagents

Iodine solution: Prepare an approximately 0.1*N* iodine solution by dissolving 12.5 g of resublimed iodine in one litre of dry carbon tetrachloride.

Mercury^{II} acetate solution: Dissolve 30 g of C.P. mercury^{II} acetate per litre of glacial acetic acid.

Sodium thiosulphate solution: Prepare approximately 0.1*N* sodium thiosulphate solution by dissolving 25.0 g of sodium thiosulphate 5-hydrate and 0.2 g sodium carbonate in one litre of water. Standardize the sodium thiosulphate solution against potassium iodate.

Starch indicator solution: Add 5 g of soluble starch which has been previously mixed with a little water to form a slurry to 500 ml of boiling water. Cool the solution and store under a thin layer of toluene.

Potassium iodide solution: Dissolve 75 g of potassium iodide in one litre of water.

Procedure

Weigh the sample, containing (2 to 7) × 10^{-4} mole of *vic*-dioxime, into a 500-ml Erlenmeyer flask. Add 100 ml of carbon tetrachloride to the sample and also to an empty flask which serves as a blank. Then add exactly 25.00 ml of the iodine solution to both sample and blank, followed by approximately 25 ml of the mercury^{II} acetate solution. If the sample does not readily dissolve, stir it in the stoppered Erlenmeyer flask until dissolution takes place. Allow approximately 30 min for the reaction to take place. Then add 75 ml of the potassium iodide solution to each flask and agitate the mixture vigorously. Titrate the excess iodine with the standard sodium thiosulphate solution, employing 2 ml of the starch solution as indicator. Observe the customary starch end-point in the aqueous layer. Calculate the results on the basis of equation (1). Table I lists the results obtained by the above procedure.

TABLE I. TITRATION OF *vic*-DIOXIMES WITH IODINE

vic-Dioxime	Sample size *moles* × 10^{+4}	Average % found
Nioxime*	5.6–7.3	99.8 ± 0.03
4-*tert*-Amylnioxime	2.4–3.3	99.5 ± 0.25
4-Methylnioxime	5.1–6.4	99.7 ± 0.07
3-Methylnioxime	3.3–4.6	99.6 ± 0.18
4-Carboxylnioxime	4.3–5.4	99.3 ± 0.28
4-Ethoxycarbonylnioxime	2.6–2.8	100.3 ± 0.15
4-*iso*Propylnioxime	2.7–3.9	100.0 ± 0.15
3:3:6:6-Tetramethylnioxime	4.5–5.7	99.8 ± 0.05
4-Octylnioxime	3.2–4.4	99.6 ± 0.20
Heptoxime*	4.8–6.6	99.6 ± 0.23
Nioxime-urea complex	3.2–4.2	98.6 ± 0.83
Dimethylglyoxime	4.2–5.4	98.5 ± 0.03
Diethylglyoxime	3.7–4.8	99.2 ± 0.26
γ-Benzildioxime	2.5–4.2	98.7 ± 0.03
β-Benzildioxime	2.1–4.1	99.6 ± 0.10

* Nioxime and heptoxime are the trivial names for 1:2-*cyclo*hexanedionedioxime and 1:2-*cyclo*heptanedionedioxime, respectively.

Interferences

The principal interferences in the titration were found to be easily oxidized materials, easily halogenated materials, primary amines, ketoximes, aldoximes, and monoximes of *vic*-diketones.

DISCUSSION

All of the *vic*-dioximes were titrated readily with the exception of α-benzildioxime, diaminoglyoxime, and α-furildioxime. The first two were insoluble in the reaction mixture and with the latter high results were obtained because of oxidation of the furane rings.

Oximes and monoximes are oxidized first to the *gem*-iodonitroso compound as indicated by the immediate blue colour formation and then are further oxidized to some higher oxidation state upon addition of more oxidant. Hydroxamic acid iodides probably result from combinations of aldoximes and iodine. Reaction conditions could not be adjusted to obtain reproducible results for the titration of ketoximes, aldoximes, and monoximes.

PREPARATION OF FUROXANES

Several of the *vic*-dioximes were dehydrogenated to their furoxane derivative in gram quantities. The melting points, boiling points, and percentage nitrogen are recorded in Table II.

TABLE II. PROPERTIES OF FUROXANES

Furoxane	B.P. at 6 mm., °C.	M.P., °C.	% Nitrogen	
			Calc.	Found*
*cyclo*Hexenfuroxane	121–122	43–44	19.99	19.56
3-Methyl*cyclo*hexenfuroxane	128–129	—	18.17	17.75
4-Methyl*cyclo*hexenfuroxane	136–136.5	—	18.17	17.98
4-*iso*Propyl*cyclo*hexenfuroxane	156–158	—	15.37	15.01
4-*tert*-Amyl*cyclo*hexenfuroxane	167–168	29–30	13.32	13.08
4-Octyl*cyclo*hexenfuroxane	—	53–54	11.10	11.28
4-Carboxyl*cyclo*hexenfuroxane	—	105–107	15.21	14.78
*cyclo*Heptenfuroxane	127–129	—	18.17	17.93
Diphenylfuroxane	—	114–115	13.08	12.87

* Nitrogen determined by the micro-Dumas method.

Procedure

Dissolve iodine, 6.3 g (0.05 mole), in 400 ml of carbon tetrachloride in a 1000-ml Erlenmeyer flask. To this add 0.0025 mole of the *vic*-dioxime to be oxidized. Add a solution of 15.9 g (0.05 mole) of mercury^{II} acetate dissolved in 250 ml of glacial acetic acid. Stir the mixture for 45 min and then transfer to an evaporation dish in a hood to permit evaporation of the carbon tetrachloride and acetic acid. When evaporation is complete extract the residue with two 150-ml portions of diethyl ether. Evaporate the ether and extract the residue again with two 100-ml portions of ether. After evaporation of the ether, repeat the process a third time. This removes most of the mercury iodide which is formed during the reaction. Dissolve the residue in a minimum of ether and vacuum distil in those cases where a liquid furoxane is obtained. If a solid is obtained recrystallize the residue from dilute aqueous ethanol and then from *cyclo*hexane.

The furoxanes listed in Table II were prepared also by oxidation of the *vic*-dioxime with sodium hypochlorite by the procedure of Boyer and Toggweiler.[7] In all cases the melting points and boiling points of the furoxanes obtained by the two different methods checked exactly. In general, the procedure given by Boyer and Toggweiler is to be preferred over the iodine reaction as a preparative method because of the difficulty involved in removing the last traces of mercury^{II} iodide from the final product.

No attempt was made to determine whether the furoxanes formed by the oxidation of the substituted nioximes with either iodine or sodium hypochlorite were mixtures or one of a pair of isomeric furoxanes of unassigned structure, *e.g.*,

Zusammenfassung—Jod dehydriert in nicht wässrigen Medien und in Gegenwart von Quecksilber(II) acetat *vic*-Dioxim quantitativ zu den entsprechenden Furoxanen. Diese Reaktion wurde zur Entwicklung einer quantitativen massanalytischen Bestimmungsmethode für verschiedene aliphatische und alicytische *vic*-Dioxime herangezogen. 15 verschiedene derartige Verbindungen wurden mit dieser Methode bestimmt und einige Furoxane isoliert sowie deren physikalische Eigenschaften beschrieben.

Résumé—L'iode en présence d'acétate mercurique en milieux non aqueux deshydrogène quantitativement les *vic*-dioximes pour donner les furoxanes correspondants. On a utilisé cette réaction pour développer une méthode titrimétrique pour le dosage quantitatif de différentes *vic*-dioximes aliphatiques et alicycliques. On a titré avec succès par cette méthode 15 *vic*-dioximes différentes. On a isolé plusieurs furoxanes correspondant a ces *vic*-dioximes et on a donné leurs propriétés physiques.

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SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM WITH THIOMALIC ACID AND THE SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

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(*Received* 12 *March* 1959)

Summary—A procedure has been developed for the ultraviolet spectrophotometric determination of rhodium with thiomalic acid. The maximum absorbance of the yellow rhodium complex is at 340 mμ; the optimum pH range is 1 to 6.

The colour is formed at 100° and the complex is stable for several days. It obeys Beer's law and is sensitive to 0.055 ppm of rhodium.

Tolerances to several ions have been established and rhodium has been determined in synthetic samples with good precision and accuracy. Rhodium and palladium in several concentration ratios have been determined simultaneously.

THERE are few satisfactory methods for the spectrophotometric determination of rhodium.[3] In most of the existing methods interferences are serious and the procedures are tedious.

The authors have recently[4] presented a method for the spectrophotometric determination of palladium with thiomalic acid (abbreviated TMA). The same reagent can be applied to the spectrophotometric determination of rhodium. The method is fairly rapid, simple and relatively free from interferences. It is also possible to determine palladium and rhodium simultaneously.

EXPERIMENTAL

Instruments

Absorbance measurements were made either with a Beckman ratio recording spectrophotometer, Model DK-2, using matched 1.00-cm quartz cells or with a Beckman spectrophotometer, Model DU, using matched 1.00-cm Corex cells.

All pH measurements were made with a Beckman glass electrode pH meter, Model G.

Reagents

Thiomalic acid[4]: A 0.05*M* solution of TMA in distilled water was prepared daily, or when needed.

Standard rhodium solution: A solution containing approximately 1000 ppm of rhodium was prepared by dissolving 0.68 g of $RhCl_3 \cdot 4H_2O$ in 250 ml of 0.33*N* hydrochloric acid. It was standardized gravimetrically[1] by precipitating the rhodium as the hydrous oxide in the presence of sodium hydroxide and sodium bromate; filtering, washing, and igniting in air to Rh_2O_3. Duplicate analyses in close agreement gave an average value of 950 ppm of rhodium. A solution containing 100 ppm of rhodium was prepared by diluting an aliquot of the standard. A few drops of hydrochloric acid were added to the aliquot before dilution in order to prevent hydrolysis.

Buffer solution: A Clark and Lubs buffer of pH 2.0 was prepared by mixing 53 ml of 0.2*N* hydrochloric acid and 250 ml of 0.2*N* potassium chloride, and diluting to one litre.

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Solutions of diverse ions: Reagent-grade salts were used to prepare solutions of the various ions. Stock solutions contained 1 mg of the ion per ml of solution.

DETERMINATION OF RHODIUM

When a dilute solution of rhodium chloride is heated at 100° with thiomalic acid, a bright yellow colour is formed.

The absorbance spectrum of the yellow TMA-rhodium complex is very similar to that of the TMA-palladium complex (Fig. 1). The rhodium complex has a maximum at 340 mμ; the reagent does not absorb at wavelengths above 290 mμ. All measurements of the complex can be made against a water "blank."

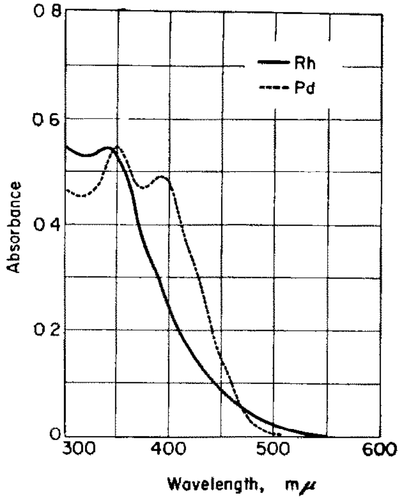

FIG. 1. Absorbance curves of the rhodium and palladium complexes with thiomalic acid.

Effect of pH

There is no noticeable effect of pH on the absorbance of the rhodium complex over the range 1 to 6. It is advisable, however, to maintain a low pH because rhodium salts hydrolyse easily.

In this study, 10 ml of a Clark and Lubs buffer of pH 2.0 were used in a total volume of 25 ml to maintain the pH close to 2.

Concentration and heating time

A boiling-water bath was employed as a source of heat for developing the rhodium complex. Addition of 1 ml of 0.05*M* TMA solution and a heating period of 40 minutes are the most favourable conditions for the formation of the rhodium complex. The complex is stable for at least a week.

Temperature

The effects of fluctuations of laboratory temperature on the measurement of the rhodium complex was studied. The temperature effect is negligible over the range of 15° to 35°.

Structure

No attempt was made to determine the structure of the Rh-TMA complex since TMA decomposes rapidly at the temperature of the complex formation (100°).

Beer's Law

The complex obeys Beer's law at 340 mμ and at 350 mμ over the concentration range 1.2 to 10 ppm, the most sensitive range being 2 to 7 ppm.

Procedure

The sample weight should be chosen so that a convenient volume will contain 50 to 175 ppm. of rhodium. Thus, a 1-ml aliquot of such a solution, diluted to 25 ml, will contain 2 to 7 ppm of rhodium.

Dissolve the sample by any appropriate method. Adjust the solution to the proper concentration range and transfer a 1-ml aliquot by means of a pipette to a 25-ml volumetric flask. Add 1 ml of a freshly-prepared 0.05*M* solution of TMA. Heat the flask in a boiling-water bath for 40 minutes, then remove and cool the flask under the water tap. Add 10 ml of a hydrochloric acid-potassium chloride buffer of pH 2.0, dilute to the mark and thoroughly mix. Measure the absorbance at 340 mμ and read the rhodium concentration from a calibration curve prepared by the same procedure.

Sensitivity

According to the Beer's law curve for the rhodium complex, a concentration of 0.055 ppm of rhodium should give an absorbance of 0.005 unit. Absorbance measurements of six solutions, each containing 0.055 ppm of rhodium, gave values of 0.005, 0.007, 0.006, 0.005, 0.005 and 0.007. Thus, 0.055 ppm of rhodium may be taken as the practical sensitivity of the method. The sensitivity according to Sandell[2] is 0.011 μg/cm^2.

Precision

The precision was determined for a solution containing 4.00 ppm of rhodium. Eleven determinations were made and the standard deviation, σ, was calculated from the formula

$$\sigma = \sqrt{\frac{\Sigma d^2}{n-1}},$$

where d is the deviation from the mean and n is the number of determinations.

$$\sigma = 0.023 \text{ ppm, } \textit{i.e.} \ 0.57\%.$$

Tolerance to diverse ions

A rhodium concentration of 4.00 ppm was used in this study. An ion was considered to interfere if it caused a difference of 0.005 absorbance unit from that containing rhodium alone.

Table I lists the tolerances to the metals commonly found with rhodium.

TABLE I.—TOLERANCE TO DIVERSE IONS (4.00 ppm Rh)

Ion	Added as	Limiting concentration, *ppm*
Platinum^{IV}	K_2PtCl_6	0.5
Palladium^{II}	$PdCl_2$	0.05
Ruthenium^{III}	$RuCl_3$	0.2
Osmium^{VI}	K_2OsO_4	1.0
Iridium^{IV}	$IrCl_4$	1.5
Gold^{III}	$AuCl_3$	0.2

Analysis of synthetic solutions

The results of analyses of synthetic solutions are summarised in Table II. All samples were run in triplicate, the averages being recorded in the table.

TABLE II—ANALYSIS OF SYNTHETIC SOLUTIONS

No.	Rh present, *ppm*	Other ions present, *ppm*					Rh found, *ppm*
		Pt^{IV}	Ru^{III}	Os^{VI}	Ir^{IV}	Au^{III}	
1	4.0	0.5	0.2	1.0	1.5	0.2	4.0
2	4.0	0.2	0.1	0.5	0.8	0.1	4.0

SIMULTANEOUS DETERMINATION OF RHODIUM AND PALLADIUM

Fig. I shows that the absorbance spectra of the palladium and rhodium complexes are similar. Rhodium does not react with TMA at room temperature. On the other hand, the palladium complex forms instantaneously at room temperature but is stable at 100°. The absorbance of both complexes is measured at the same pH. Experiments showed that the absorbances of the palladium and rhodium complexes at 350 mμ are quantitatively additive.

A number of synthetic samples of known concentrations of palladium and rhodium were analysed in order to test the proposed method and to determine the maximum practical variation which could be allowed in the ratio of palladium to rhodium for their simultaneous determination. Ratios from 1 : 1 to 60 : 1 palladium to rhodium can be determined successfully (Table III).

TABLE III.—SIMULTANEOUS DETERMINATION OF PALLADIUM AND RHODIUM

No.	Pd added, *ppm*	Rh added, *ppm*	Pd Found, *ppm*	Rh Found, *ppm*
1	3.0	3.0	3.1	2.9
2	4 0	2 4	4.1	2.3
3	4.0	2.0	4.0	2.0
4	4.0	1.2	4.0	1.2
5	5.6	0.4	5.6	0.4
6	6.0	0.1	6.0	0.1

Procedure

The sample weight should be chosen so that a convenient volume will contain at least 50 ppm of palladium but not more than a total of 175 ppm of palladium and rhodium.

Dissolve the sample by any appropriate method and adjust the solution to the proper concentration range.

Palladium: Transfer a 1-ml aliquot by means of a pipette to a 25-ml volumetric flask. Add 1 ml of a 0.05*M* TMA solution and 10 ml of a hydrochloric acid–potassium chloride buffer of pH 2.0. Dilute the solution to the mark and mix thoroughly. Then measure the absorbance at 350 mμ and read the palladium concentration from a calibration curve prepared by the same procedure.

Rhodium: Transfer another 1-ml aliquot to a second 25-ml volumetric flask and treat as outlined above in the procedure for rhodium. Measure the total absorbance at 350 mμ and calculate the absorbance due to the rhodium complex.

$$A_s \text{ total} - A_s \text{ Pd} = A_s \text{ Rh}$$

Read the rhodium concentration from a Beer's law curve prepared for rhodium at 350 mμ.

CONCLUSIONS

Thiomalic acid has several advantages as a reagent for the spectrophotometric determination of rhodium: It is colourless and water soluble; no extraction of the metal complex is required; the pH for maximum absorbance is easily controlled; iridium interference is not serious and palladium may be determined in the same sample; the method is simple and sensitive and its precision and accuracy are good.

Zusammenfassung—Es wurde eine UV-spektrophotometrische Methode zur Rhodiumbestimmung mit Thiomaleinsäure entwickelt. Das Absorptionsmaximum des gelben Rhodiumkomplexes liegt bei 340 mμ, und der günstigste pH-Bereich bei 1–6. Die Farbe wird bei 100°C gebildet und ist mehrere Tage beständig. Das Beer'sche Gesetz wird befolgt. Die Empfindlichkeit beträgt 0,055 ppm Rhodium.

Der Einfluss mehrerer Ionen wurde untersucht und Rhodium in synthetischen Proben mit guter Übereinstimmung und Genauigkeit bestimmt. Rhodium und Palladium konnten in verschiedenen Konzentrationsverhältnissen gleichzeitig bestimmt werden.

Résumé—On a développé une méthode de dosage spectrophotométrique dans l'Ultra-violet du rhodium par l'acide thiomalique. Le maximum d'absorption du complexe jaune du rhodium est à 340 mμ; le domaine de pH le plus favorable est 1–6. La coloration est obtenue à 100° et le complexe est stable pendant plusieurs jours. La loi de Beer est suivie et la sensibilité est de 0,055 ppm de rhodium.

La présence de plusieurs ions peut être toléré et le Rhodium a été dosé dans des échantillons synthétiques avec une bonne précision. Le rhodium et le palladium, présents en proportions variables, ontété dosés simultanément.

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A CRITICAL EVALUATION OF SPECTROGRAPHIC, FLUORESCENT X-RAY, AND POLAROGRAPHIC METHODS FOR THE DETERMINATION OF THE PLATINUM METALS

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Summary—This review covers pertinent publications up to June 1958. The methods are evaluated from the point of view of their analytical applications to assay beads and buttons, platinum metal precipitates, and alloys of platinum metals with and without base metal impurities.

No spectrographic method has been recorded for the direct determination of platinum metals in ores or concentrates. For the determination of palladium, platinum and rhodium in ores and concentrates the most accurate spectrographic methods involve a preliminary fire assay extraction to produce a lead button or a silver bead. For these, and for other alloys, precipitates, etc. the most accurate methods involve special efforts to produce uniformity of composition and to produce standards with identical metallurgical histories. No successful spectrographic method has been recorded for either the direct or indirect determination of iridium, ruthenium and osmium in ores, concentrates or complex alloys.

None of the frequent claims that spectrographic methods produce greater accuracy than wet methods has been substantiated and all are unacceptable. The few existing data indicate that with competent analysts and under optimum conditions the accuracies of the two methods are comparable.

For the qualitative examination of the purity of precipitates etc. containing a variety of metal traces the spectrographic method is incomparably superior to wet methods.

Polarographic methods for the platinum metals have been confined to systems with few constituents. No procedure has been recorded for the successful application to assay beads or buttons. Few detailed procedures have been recorded for the determination of any platinum metal and no method includes the usual processes of securing dissolution of multicomponent systems. Undoubtedly, polarographic methods could be useful competitors in areas below those in which classical methods apply. Furthermore, both spectrographic and polarographic methods provide the great advantage of speed when applied to large numbers of samples whose compositions are not widely different.

Too few X-ray spectrographic procedures have been recorded to estimate relatively their accuracy and precision.

Practically the whole of the world's supply of the platinum metals is derived from ores whose precious metal content is close to or below the limit of detection of the most sensitive analytical methods. No direct method has been recorded for the quantitative or even the qualitative determination of any of the six platinum metals in ores. The lack of qualitative and field detection methods is, in the author's opinion, due to a lack of effort or interest on the part of the analytical researcher. The absence of direct quantitative procedures is, of course, due partly to the same situation, and partly to a strange tendency, on the part of the analytical researcher, to distinguish, and thus to avoid, these analytical problems by creating the artificial classification of fire assaying. For the relatively few engaged in this work, the high specificity of spectrographic methods has encouraged a persistent hope that this approach to platinum metal determinations may provide the much desired easy and positive application to ores. However, despite some rather extravagant claims, no proved direct spectrographic application has been recorded; nor is one of general value likely to be evolved within the forseeable future. The spectrographic methods available have been used largely for alloys of the platinum metals. Those of significant analytical value for the determination of platinum metals in ores have been applied, almost exclusively, subsequent to concentration by fire assay or other means. However, in the author's opinion, no analytical method provides the general efficiency attained by spectrographic procedures for the detection and determination of impurities in platinum metals alloys. In some cases colorimetric methods may provide comparable or even greater sensitivity and accuracy but only at the expense of more difficult techniques and the greater expenditure of time.

For those alloys, such as the silver bead or lead button, whose proportions of platinum metals are small, the relative accuracy and precision of spectrographic and spectrophotometric methods, a problem of some practical importance, has not been determined over sufficient ranges of concentration; the rather persistent claims for superiority of the former method must be dismissed for lack of evidence. Not a single publication has provided results to support these claims. However, one can predict with confidence that where both methods may be applied at all, competent operators will find comparable platinum metal values and the few results recorded[1,2] indicate this to be the case.

The general applications of the spectrograph for the determination of platinum metals as trace constituents are wide and invaluable. Gorbach and Windhaber[3] used the method to find traces of palladium, iridium, platinum, silver, etc., in Forest Honey. Fothergill, Withers and Clements[4] determined traces of platinum and palladium in the atmosphere of a platinum metals refinery. The author will make no attempt here to discuss the innumerable reports dealing with the spectrographic detection and determination of the platinum metals in all of their applications. This review will be concerned with the analytical treatment of assay beads and buttons obtained from platinum ores and concentrates; with alloys of which, at least, the principal constituent is one of the platinum metals; and with the determination of the purity of precipitates of the platinum metals.

SPECTROGRAPHIC METHODS

Preparation of electrodes and samples

As would be expected the choice of electrode material is sometimes determined by the physical character of the sample to be analysed and frequently by the necessity of avoiding a multiplicity of interfering lines. For aqueous and certain solid samples the most common choice has been the graphite electrode. The positive rod is drilled to receive the liquid which, by intermittent evaporations, may contain a large sample. The cavity may sometimes be coated with wax or other water-impervious materials to prevent diffusion beyond the area of effective electrical contact. The upper electrode is frequently sharpened to assist in the concentration of the electrical contact and to avoid wandering of the projected image beyond the slit area. For liquid samples various mechanical devices have been reported which permit each of a series of graphite rods to make regular and intermittent contact with the liquid sample; *e.g.* the rotating pin electrode technique which was recommended by Bardoćz and Varsányi.[5] With this method the ends of the carbon electrodes were fastened like spokes on a slowly rotating horizontal shaft and were arranged to pass before a carbon counter-electrode. The solution to be analysed, into which the carbon rods dipped, was placed on a vertically adjustable shaft. The movement was timed by an adjunct device arranged to create the discharge only when one of the electrodes just passed the counter-electrode. The usual warming up phenomena associated with porous-cup techniques involving high energy excitation and with rotating disk techniques was reduced to an acceptable degree.

For solid samples various metallic electrodes have been used to which an alloy sample may be fastened mechanically or incorporated chemically; or the alloy sample may itself serve as the electrode.

Pasveer[6] converted the powdered standards to pellets, which were then annealed. The solid sample was rolled into sheet from which a disc was cut and fitted over a rod to duplicate the shape of the standard electrode. Pellet electrodes were also used by Hawley, Wark, Lewis and Ott[7] who mixed palladium or platinum black, prepared from solution by reduction with aluminium, with briquetting graphite. The mixture was compressed in a steel mould at 10,000 psi and the pellet was mounted in a brass adapter on the arc-spark stand. To produce a spark spectrum from a silver assay bead, Seath and Beamish[8] used a silver cup made from foil, inserted in one end of a glass tube and attached beneath, through a tube, to the lower terminal of the spark stand. The upper negative electrode was a gold wire. This equipment facilitated the removal of beads. The spectrographic method reported by Scobie,[9] one of the first generally useful procedures, involved the arcing of a silver assay bead containing platinum, palladium and rhodium. This author examined the applicability of various metal electrodes, rejecting cadmium, tin and zinc because of low melting points, copper because of mechanical failure, and steel and brass because of poor heat and electrical conductivity, and chose a silicon-copper rod. The upper electrode was graphite sharpened to give an end comparable in area to the 100-mg silver bead. The latter was cleaned, placed in a mould designed to allow deep punching of the silver bead at an included angle of 30°, and transferred to the copper electrode previously pointed at the same angle.

To achieve uniformity of composition in samples Lewis[10] fused silver- and gold-lead buttons under hydrogen. By this method platinum, palladium and rhodium were thus uniformly dissolved. Unfortunately the procedure has not yet been extended to include iridium and ruthenium. The lead alloy button thus prepared was mounted on a copper rod by pricking several small holes in the end of the rod with a sharp centre punch; the button, covered by a strip of heavy aluminium foil, was placed on the end of the rod and tapped lightly until flattened sufficiently to cover the end of the rod. The button was thus retained by filling the depressions in the copper rod. Lewis, Ott and Hawley[11] recorded interesting results concerning the relative efficiency of various standard methods of preparing samples together with electrode material. For the determination of impurities in rhodium they used rhodium solutions with both coated-electrode and porous-cup techniques. Solutions were evaporated in the flat end of electrodes of lead, zinc, aluminium, copper, mercury-coated copper, graphite, collodion-coated graphite, and Kerosene-impregnated graphite. The object was to find an electrode material on which the solutions would either plate or form a homogeneous salt layer. Most of the systems were rejected. Various metals reacted with rhodium solutions to form objectionable salt mixtures. Coated or impregnated graphite electrodes resulted in thick and brittle salt layers. When the proportions of contaminants were high a salt crust formed on copper or mercury-copper electrodes, although in some cases plating did occur. Sensitivity was poor with copper electrodes. Under certain circumstances porous-cup graphite electrodes, wrapped in aluminium or lead foil, were sufficiently successful for chloride solutions of rhodium and for the contaminants iridium, palladium, iron, nickel, lead and silver. In the case of gold there was, as would be expected, some precipitation, which could be avoided to a degree by the addition of *aqua regia*, although the latter introduced corrosion of the clamps. The above difficulties, together with the necessity of long exposures to achieve adequate sensitivity were objectionable features of the carbon porous-cup techniques. The advantages were ease of obtaining uniformity of composition, good precision, and the facility with which standards could be prepared.

A fusion method which produced acceptable uniformity for the determination of palladium in a high-proportion silver alloy was described by Tomingas and Cooper.[12] The method involved prior fusion of silver-palladium alloys with the silver alloy to be analysed; or when copper was to be alloyed, addition of the latter in the form of wire to the base of the carbon crater, followed by the silver alloy; and subsequent pre-arcing for 30 seconds.

Platinum metals in ores and concentrates

The assay bead: While no spectrographic procedure for the direct determination of platinum metals in ores has been recorded within the past two decades, various spectrographic methods have been developed for these determinations subsequent to extraction from liquid solution by metals from whose line spectra there is relatively little interference. The extraction is usually arranged to provide the necessary degree of concentration of platinum metals and is generally accomplished by standard fire assay methods. The spectrographic techniques which have been used for these alloys are not unique; with the exception of a few novel methods of producing sample-electrode contact, the procedures are those previously accepted for general spectrographic applications. The improvement of methods for the platinum metals has followed chronologically the evolution of these spectrographic techniques in general. Laszlo[13] used the simple technique devised by Kiess and Stimson[14] of relating the concentration of platinum in silver assay beads to the disappearance of certain platinum lines in a condensed spark spectrum; the last ones to disappear were designated as *raies ultimes*. The method involved the preparation of standard silver-platinum electrodes containing 5% to 0·01% platinum, creating a condensed spark under identical conditions for a measured time and ascertaining the number of the platinum lines from each alloy. The silver beads were prepared by cupellation and by a fusion process. Care was taken to ensure alloys of uniform composition. The beads were cut in half and the flat side of each hemispherical section was soldered to a short piece of brass wire thus forming the electrode. An accuracy of about 20% was obtained, but the method was unsatisfactory for concentrations of less than 0·04%. Neither this spectrographic technique nor the method of bead preparation are recommended. The former is unnecessarily tedious and the latter could not be used successfully with the normal assay bead where uniformity of composition is seldom, if ever, attained, particularly when the more insoluble platinum metals are present. A similar objection can be made to the method of Peters[15] who gave directions for the collection by fusion with lead acetate and subsequent cupellation. The claim that the volatilisation of osmium was prevented by partial cupellation can be accepted only with reservations.[16] Determinations were made for silver, gold and the six platinum metals. Seath and Beamish[8] had little success with the above spark method applied to assay beads containing platinum and palladium. They found the arc spectrum less sensitive to variations in electrical conditions, and since small beads were consumed the problem of non-uniformity of alloy composition was of much less significance. These authors preferred graphite electrodes and silver beads of about 10 mg. Threshold lines for arc and spark spectra of silver and gold beads and their corresponding limits of concentration of platinum and palladium were recorded. The work was essentially qualitative and a claim was made for a sensitivity on 10-mg silver beads of 0·04 μg of platinum or palladium, which is beyond that usually accepted. The relative sensitivity of arc excitation and chemical methods for ores was discussed by Azcona and Pardo.[17] The former was considered superior when applied to concentrates obtained by cupellation or electrolytic methods. The authors used a molybdenum line as an internal standard and recorded a sensitivity of about 0·5 μg for platinum, palladium, ruthenium and gold; and about 200 μg for iridium.

The adverse influence of copper on the spectrographic determination of palladium in Doré Metal and silver assay beads was described by Tomingas and Cooper.[12] The Doré Metal contained 90–95% silver, 5–10% gold, 0·3–0·8% platinum and 45–80 ppm of palladium. An AC arc was used with carbon electrodes, the upper cone-shaped and the lower with a crater, and solid samples. It was found that copper in excess of 0·4% influenced the intensity of both the silver line 3469, used as the internal standard, and the palladium lines; furthermore the fluctuations in copper content eliminated compensation by the silver and also compensation by the background method. A relatively high lead concentration was also objectionable since it resulted in sputtering during the arcing and low palladium results. Generally the lead proportion could be reduced by a pre-exposure or by subsequent addition of silver to the silver bead, kept small initially for this purpose. The deleterious effect of copper was met by establishing separate working curves constructed from the palladium:silver intensity ratio with sets of alloys containing appropriate amounts of copper. The applicable curve was determined by the copper:silver line ratio. The standards were prepared by melting and shotting Doré drillings containing 0·4% to 0·5% copper. Palladium, as required, was incorporated by addition of a palladium-silver alloy and subsequent melting. Copper was alloyed by placing the required weight in wire form on the bottom of the carbon electrode crater, adding the Doré metal, and subjecting the mixture to a 30-sec pre-exposure. Samples to be analysed and requiring salting with copper, etc., were similarly treated to ensure uniformity of composition and metallurgical history. In practice the sample was excited and viewed visually for evidence of a green colour before analysis, to determine if the copper content was below 0·4%, in which case the palladium lines were too weak for measurement. Gold, in concentrations greater than 9%, interfered with the palladium determination. The accuracy of the method, as compared to polarographic methods (unfortunately these were not described), indicated very acceptable uniformity of the alloys prepared by the prescribed fusion methods. The method was recommended for the determination of palladium as low as 0·05 ppm in ores, concentrates, blister copper and other metallurgical products. Various Russian analysts[18–20] have used copper sulphide as a collecting medium for platinum, palladium, gold, etc., to produce finally a copper pearl which was then analysed spectrographically. Van'kin and associates[18] precipitated by sodium thiosulphate. Bufatin and associates[19] separated platinum and palladium from uranium by hydrogen sulphide in sulphuric acid solutions, with copper sulphide as the collector. For the spectrographic analysis gold was used as the internal standard; line 2675·95 for gold against 2659·45 for platinum; and line 3122·78 for gold against 3421·24 for palladium. Livshitz and Kashlinskaya[20] used thiosulphate to precipitate the sulphides of platinum, palladium, rhodium and gold, together with copper added in amounts to produce a final bead of 100 to 200 mg. Prior to extraction by a variety of mineral acids the sample was treated to concentrate the platinum metals. Unfortunately the authors provide no data concerning the efficiency or the character of the concentrating process. Furthermore the statement that the maximum loss of platinum metals due to deficiencies in the wet extraction was less than 5% can apply only to the samples examined; such dissolution procedures can result in serious losses. The copper bead containing as little as 5 μg of platinum metal was placed in a depression on the lower carbon electrode and subjected to an alternating arc of 220 volts and 4·0 amps. The copper line, 2445·0 was used for comparison with 2675·95 for gold, 2659·45 for platinum and 2447·91 for palladium. For rhodium 3434·89, the copper comparison line was 3375·67. The few results reported indicated a good recovery for samples containing very small amounts of the platinum metals. Excluding the possibility of misinterpretation through translation, it would seem that the proposed spectrographic method involved amounts of the platinum metals considerably below the sensitivity generally accepted. The authors make the usual claim for superiority of accuracy over wet methods, with the usual omission of any description of the character of the methods or any acceptable data. It is a fact that the amounts of platinum metals involved in the analysis falls well within the range of the most acceptable spectrophotometric methods. Presumably the tendency toward these unsubstantiated claims is not confined to regional literature and in this instance, as in all others recorded in this review, there is the suggestion that the wet methods were uncritically chosen, incorrectly applied, or applied by operators lacking in efficiency. It may be well to suggest here that these authors' approach toward spectrographic analysis for the platinum metals through the preparation of a copper bead offers good promise if it can be incorporated within the new scheme involving a collection from ores by iron-copper-nickel buttons.[1,2]

Scobie[9] used a low voltage AC arc method for the spectrographic determination of platinum, palladium, rhodium and gold in ores subsequent to collection of silver beads. Standard beads were prepared from standard platinum metals and silver solutions evaporated in lead boats, and the residue was subsequently cupelled. The upper graphite electrode was pre-burned for a period of 2½ minutes. A pre-arcing period of 30 sec was considered desirable followed by a 2-min exposure period. Intensity measurements of the appropriate platinum metals lines were made relative to the background of silver line 3233·25. Continued routine practice indicated this procedure to be superior to that of line compensation. The range of concentration, 0·001% to 0·1% of platinum and palladium, was covered by one line and for rhodium by two lines. The author claimed a sensitivity of 1 μg of platinum metals per assay ton of ore, with the probability of increasing this to 0·1 μg. All of the precious metals could be determined by one spectrographic arcing with an accuracy of about 5% average deviation from absolute values. The author's claim that the procedure offered the advantage of speed over existing wet methods of platinum metals analysis is beyond dispute but the claim for greater accuracy was not substantiated and is unacceptable. A conclusion such as this, too frequently made in spectrographic literature of the platinum metals, loses any significance when comparisons are made with wet methods, the character of which is not described, and the source of the data being unstated. In the present instance the author offered no data for platinum metals values obtained by wet methods. The author's calculations of accuracy and precision, were, in some cases, incorrect and the claim of a 6% accuracy is well on the optimistic side.

Presumably Scobie found no difficulty attaining uniformity of composition with the silver beads. In the case of platinum, palladium, and to a lesser degree, with rhodium, careful fusions with lead and silver may result in a uniform distribution of these three platinum metals. However, later investigators have encountered evidence of some segregation, with the result that one cannot now accept without reservations the direct application of spectrographic spark methods to assay beads. Low voltage arc methods in which beads are entirely consumed may avoid the difficulty but suitable quantitative procedures have not been recorded. Hawley, Lewis and Wark[21] applied a low voltage spark method to determine the platinum and palladium content of minerals and ores. The difficulties of assuring uniformity in the normal assay bead and in standards was avoided, in the latter case, by the preparation of a gold-mercury-platinum or palladium amalgam subsequently dissolved and reduced by zinc, in the former case by the normal assay fusion and cupellation to produce a gold-platinum-palladium bead, followed by weighing and, as in the case of standards, by dissolution in acids and reduction by zinc to produce platinum and gold precipitate. Subsequent to the purification of the black precipitate the latter was treated to form a mercury amalgam in the same manner as the standards. For spectrographic determination gold lines were used as the internal standard. This paper will be of considerable interest to those concerned with the mineral origins of platinum and palladium. Rhodium, iridium, ruthenium and osmium were not detected in the minerals examined. Presumably the authors did not consider that their wet treatment of the gold bead could eliminate these four elements from subsequent detection by spectrographic analysis.

A method for the spectrographic determination of platinum, palladium and rhodium in ores, slimes and tailings was recorded by Nedler.[22] The procedure involved a fire assay to produce a silver bead, division of the bead and shaping each section to form a cylinder tipped to a dull wedge, excitation between these two sections by a high voltage spark, measurement of line length relative to silver lines by a logarithmic sector, and the application of a correction curve derived from a silver fixation line pair correlated with concentration errors and made necessary by wide variations in excitation conditions. For platinum determinations five line pairs were required for the range 0·02%–1%, for palladium three line pairs over the range 0·2%–1%, and for 0·2%–1% of rhodium, two pairs. The method introduces no new principle and in the opinion of the present author is cumbersome, relatively inaccurate and inapplicable to those materials which contain iridium, ruthenium and even large proportions of rhodium. While the author commendably recognises the difficulties arising out of irregular distribution of platinum metals in ores, the deleterious effects of variations in the metallurgical history, size, shape, etc. of the silver alloy electrode, he suggests very little to overcome most of these problems. The use of a fixation line pair to arrive at a correction factor to reduce errors of the order of 50% to 10% or 15% is scarcely an encouraging feature. The failure to recognise that a silver assay bead is seldom free of interfering impurities may be excused by the acceptance of a 10%–20% inaccuracy but it is not a recommendation for the technique used in view of the fact that modifications may be used to produce a greater accuracy. The physical method used to shape the silver alloy electrode is objectionable and can be accepted with reservations only when one is assured of homogeneity, a factor which received inadequate attention. The inclusion for comparison of the results of wet methods of analysis is an excellent feature and an improvement over many of the more acceptable spectrographic publications, but it is regrettable that the wet methods were not identified. The author's justification for the acceptance of a 10%–15% precision, on the grounds of as much as an 80% heterogeneity of platinum metals in ores, is acceptable only with considerable reservations.

Lead button. In a later paper Hawley and co-workers[23] stated that the above mercury amalgam method[21] sometimes failed to provide uniformity. The proposed new method involved the formation of a platinum metal alloy with enough lead to reach a concentration of platinum metals falling within the sensitivity range of the spectrographic method. Obviously this might be most readily accomplished by a carefully controlled cupellation. However, the normally associated base metal content of a partially cupelled lead button introduced objectionable interferences. The author's fire assayed the ore samples in the normal manner, adding gold or silver as a collector in amounts which provided "weighable gold or silver beads". The latter, together with sufficient lead to constitute 90% to 95% of the resulting alloy, were fused on a charcoal block, weighed to determine the lead content and fused with solder to a copper electrode. There was no appreciable interference from the solder. Master standard beads, containing the required ranges of concentration of gold or silver and platinum metals were prepared by a similar fusion on a charcoal block. Subsidiary standards and beads simulating the composition of silver assay beads were prepared by suitable dilutions and fusions with lead. Variations in lead content and high silver content did not affect the spectrographic determinations. High gold content affected adversely the results from the lead button. The spectrographic analysis was made with a 15,000-volt condensed spark and calculations of concentration were based on the mutual or variable internal standard method. This procedure involved the determination from the alloy standards of working curves recording intensity ratios to either of two lead lines of each of appropriate lead, gold, silver, palladium, platinum, rhodium and bismuth sensitive lines. For assay beads, converted to lead alloys, the working curves permit a determination of the relative per cent of each constituent of the lead alloy, which in turn allows a calculation of the total lead content. This must agree within experimental error with the amount of lead as determined by direct weighing of the lead added to the assay beads. With this condition satisfied the per cent of each platinum metal is readily calculated in suitable terms. The sensitive lines used for the determination of the ratio of element to lead were arc lines with a few exceptions although a condensed spark was applied to the electrodes. The precision of the method was about 6%. The size of button or electrode was without any appreciable effect on the accuracy of the method. The accuracy attainable, determined from salted samples, indicated a recovery for palladium, platinum and rhodium within about 5%. The accuracy of recovery as determined on assay beads prepared from ores was not determined. In its present form the method will not prove applicable to such assay beads containing iridium, ruthenium or osmium. Iridium is collected mechanically by lead and hence uniformity of composition will not normally be achieved. Ruthenium, sometimes incorrectly described as volatile in a lead button, may offer both mechanical and spectrographic difficulties. Osmium is largely lost during cupellation to form a silver or gold bead. Indeed, with large proportions of osmium in a silver assay bead, the latter will explode violently. Hawley and Rimsaire[24] applied the above techniques to the determination of Canadian uranium and sulphide ores. Tentative results are included for ruthenium, iridium and osmium. The authors acknowledge the deficiency of their method for these three metals. The sensitivity of the authors' method based on the lead collection from one assay ton of ore with the production of a ten-mg lead bead was reported to be 0·003 ppm for platinum and 0·0008 ppm for palladium and rhodium. These values are not supported by results and cannot be accepted without verification. Here it is well to realise that the accuracy of methods such as the above and the related methods described below, applied to assay beads from ores or concentrates, may be subject to errors not discussed by the various authors. Where ores contain an unusually high amount of platinum metal "insolubles", the latter may well include alloys, resulting from the heat treatment or occurring in ores as minerals, which contain proportions of platinum, palladium and particularly rhodium. To the degree that these "insolubles" are present, there may be some lack of uniformity in the distribution of the above three metals. In practice the proportion of "insolubles" is usually very small in which case the error would be insignificant.

There is a further condition which can lead to errors in these methods which depend upon uniformity of bead or button composition. The collection of platinum metals by silver or gold is accomplished at elevated temperatures, during which period metals such as rhodium or its alloys will, in some cases, become resistant to corrosive reagents which normally encourage dissolution processes. One cannot assume that rhodium in this condition will become uniformly distributed, particularly when the proportions in the bead are large.

Lewis[10] examined critically the spectrographic determination of platinum metals in lead buttons obtained by a variety of fire assay methods applied in a number of different laboratories. This excellent reconnaissance survey not only provided assurance of the practical efficiencies of fire assay techniques but included a description of the most acceptable procedure for the preparation of platinum, palladium, rhodium-lead alloys so far recorded.

Master standards were prepared by fusing macro amounts of the platinum metals under hydrogen to produce alloys containing either 5% gold or 10% silver together with platinum, palladium and rhodium from 0·001% to 1·0%. Working sets of either gold or silver standards were made by diluting the master standards. For analysis, the gold or silver fire assay beads were fused under hydrogen with sufficient lead to produce the 5% gold or the 10% silver-lead alloy.

The samples were mounted on copper rods as described above under electrode preparation and sparked with a high-voltage spark from a High Precision Source unit. Intensity ratios of platinum metals, gold and silver were calculated with lead as an internal standard. The dissimilarity of physical properties of lead and precious metals produced no appreciable error in measurements of relative intensity.

The analysis of precipitates and commercial alloys

Spectrographic methods are, in general, incomparably superior to all chemical procedures for the detection and, to a lesser degree, for the determination of metal impurities in precipitates. In those cases where the impurity is one of the more insoluble platinum metals the great advantages of the spectrographic analysis is obvious, as it is also when precipitates may contain traces of a number of metals. Usually this analysis is essentially qualitative and one spectrogram will suffice for the whole gamut of metal impurities. The problem of attaining uniformity can often be avoided by acceptable precipitating procedures. However, where accurate measurements of impurities are required and where a high voltage-low amperage spark excitation is used, the analyst will do well to recall that the processes of contamination of precipitates are not always conducive to uniform distribution. This possibility has, to the author's knowledge, received no recognition in the various publications dealing with these determinations. Perhaps it is not too irrelevant to refer here to the growing practice of evaluating the efficiency of a standard gravimetric procedure by a spectrographic examination of the precipitate and the corresponding filtrate for the distribution of constituents. Particularly in those instances where the completeness of recovery is sensitively related to conditions of precipitation, such investigations may result in an evaluation of the operator as much as, or more than, in an evaluation of the procedure. In any case the practical efficiency of an analytical method is usually much more effectively determined by a reconnaissance survey than by the results obtained by an isolated investigation. However, one cannot over-emphasise the usefulness of spectrographic methods in determining the purity of precipitates nor the need for this information when new methods are proposed.

For the detection of impurities in solids the arc method of excitation is generally the most sensitive. Typical of the procedures for a general examination of impurities in solids is that described by Raper and Withers[25] who used the arc with graphite electrodes, the lower of which contained a cavity to hold the platinum sample. Spectra were photographed, first of the pure platinum, then of the sample, and finally of *R.U.* powder, on a plate on which the wave length scale was printed. The authors recorded the lower limits of detection in percentage by weight of silver, lead, nickel, palladium, iron, ruthenium, arsenic, antimony, rhodium and iridium.

In a series of papers Ayres and co-workers[26–29] provided spectrographic procedures for the determination of palladium, platinum, rhodium and iridium in samples containing as low as 5 ppm of a single platinum metal. The problem of uniformity was avoided by using aqueous-acid solution. A high voltage spark source, altered by an increase in the inductance of the spark circuit to give more arc-like excitation, was used and the porous-cup graphite electrode was recommended. Cobalt was added as the internal standard and line pairs of the platinum metals used with the cobalt line 3354·2 were included. The authors varied the relative concentrations of the platinum metals over wide limits and reported an accuracy of 2·8% and 2·4%

average deviation of the intensity ratios. A 180-sec exposure was required for an acceptable sensitivity. Because of variable porosity, pre-sparking of the electrodes was necessary. Within the concentrations recommended, the line intensity ratio of one platinum metal was unaffected by variations in concentrations of the remaining two metals. Ayres used these or related procedures for the evaluation of the efficiencies of standard separations of palladium from platinum, iridium and rhodium,[26] of rhodium from iridium[27] and of platinum from palladium, rhodium and iridium.[28] The lower limits of detection were 5 ppm for palladium, 20 ppm for platinum, 10 ppm for rhodium and 25 ppm for iridium.[29] For the investigation of the rhodium-iridium separation by titanium^{III} chloride the lower limits of detection were 0·5 ppm for rhodium and 50 ppm for iridium. Smaller amounts of iridium were determined spectrophotometrically. For the evaluation of the platinum isolation by hydrolytic separation[28] the authors used a direct current arc excitation with carbon rods, the lower of which was shaped to form a cup and the upper sharpened to a point. The dry sample together with the cobalt salt was mixed with carbon, and the mixture in the graphite cup was covered with lithium carbonate to prevent mechanical loss and to reduce the cyanogen band background. The spectrochemical method showed a precision of 4·7% and an accuracy of 5·3%. The authors stated that there was a slight compensation of errors, which were insignificant except where the amounts of the metals were 20 mg or less. Van Der Voort[30] prepared platinum and palladium by standard procedures and discussed the relative advantages of various methods of excitation for determining the palladium content of platinum. With arc analysis the palladium spectrum decreased in intensity with time. The interrupted arc was useful if the platinum retained its form but the accuracy was not great. The spark excitation was suitable for larger amounts of metal containing 0·1% of palladium or more. Under certain conditions a glow discharge at atmospheric pressure with a current of 0·25 amp at 370 volts was promising.

In order to attain uniformity of composition and grain size, Hawley and co-workers[7] utilised precipitation methods for the determination of impurities in platinum and palladium sponges and refinery samples. The samples were dissolved by standard procedures and treated with aluminium to produce the finely divided "black." Standards of suitable purity were similarly dissolved, salted with the appropriate impurities and similarly precipitated. The black precipitates were mixed with carbon, compressed to form pellets and, with the major constituent serving as an internal standard, analysed spectrographically with excitation by a Multisource spark discharge. The range of concentrations of impurities were those common to refinery samples. The accuracy of the methods was of the order of 3%. The authors were of the opinion that spectrographic analyses yielded "a much higher degree of accuracy than the chemical analyses".

Inexplicably, this claim of superior accuracy is repeated in various publications. Statements to the effect that spectrographic methods for the determination of minor contaminants are "far superior to wet chemical methods and should be used, if not exclusively, as a check in the chemical determinations" really mean that a purely empirical analytical procedure should be accepted as the primary standard.

Lewis and Ott[31] found good agreement between their "black" technique and a method involving the preparation of palladium sponge. The direct analysis of platinum metals sponges was rejected because of the probable lack of homogeneity, the difficulty experienced in properly salting spectrographic standards and in duplicating metallurgical history. These difficulties were overcome by dissolution of both samples and standards, salting the latter with appropriate metals, evaporation to salts, mixing in a mortar, reduction to sponge by hydrogen, mixing again in a mortar and reducing again with hydrogen. The sponge was then mixed with graphite, and pellets were prepared by a modification of the method discussed above.[7]

Excitation of the pellet was accomplished by a high-voltage spark, and various filters were used to reduce the intensities of lines of such impurities as gold, silver and copper. The addition method of analysis[32] was used except where the proportion of the contaminant was 0·005% or below, in which case spectrographically standardized palladium sponge was used. The authors preferred the more practical "analytical samples" as standards and by prior examination chose the sponge containing the lowest degree of contamination. After the determination of the proportion of the residual contaminant, true concentrations were plotted on logarithmic paper against intensity ratios of the chosen line for the contaminant and a palladium line as the internal standard. The authors' results, which indicate excellent precision and accuracy, reveal also the peculiar tendency to values higher than those indicated by "check" samples. There were no indications of elements which could depress the intensity of spectral lines. It was concluded that while, in general, comparable results were obtained by the "black" and "sponge" techniques, the former was superior for the determination of silicon, lead, bismuth and iridium. Of particular significance is the conclusion that the sensitivity of methods decreases in the order, "black," "sponge," "solution" and finally, "salt" methods. The "sponge" and "black" procedures were also examined, with the former prepared as described for palladium and the latter prepared by reduction in alkaline medium, by hydrazine dihydrochloride. The resulting pellets, prepared as described above[7], were excited by a high-voltage spark discharge in the case of the "sponge" and by the direct current arc in the case of the "black". To determine silica a modified "sponge" procedure is described in which the addition method of analysis is used. The precision obtained for the impurities varied between 2% and 7%. With direct-current arc discharges the precision was of the order of 15%. The authors concluded that the "sponge" technique was most suitable for the determination of iridium, palladium, iron and copper. The preparation of the black was preferred for other impurities. Further application of the "sponge" and "black" techniques was recorded by the authors who examined rhodium spectrographically for iridium, palladium, platinum, ruthenium, copper, nickel, cobalt, silver, gold and silica.[11] The samples and standards were prepared as described above.[11]

A procedure for the determination of rhodium in platinum alloys was discussed in an interesting and useful paper by Bardocz and Varsányi.[5] The range of concentrations investigated was about 0·5 to 12% of rhodium in platinum. Because of the difficulty in duplicating size, shape and metallurgical history in the standards and samples, the authors preferred to work with aqueous solutions and in order to avoid the deleterious effects of warming up of the solutions on the electrodes and also to permit a continuous feeding process, the rotating pin technique, described above, was applied. Both arc and spark excitation methods could be used. The porous-cup electrode was unsatisfactory due to lack of precision caused by varying porosity; pre-exposure of the electrode only partially corrected the difficulty.

Furthermore the porous-cup technique limited the choice of excitation methods, eliminating the higher sensitivity energy spark discharge because of the tendency toward excessive heating. For the same reason the rotating-disc technique was rejected, although here the problem of porosity is avoided. The relative warming effects of the rotating-pin and rotating-disc methods were well illustrated. For the determinations the author used a low voltage condensed spark source directed electronically at 1000 volts with an effective pre-sparking time of 7·5 sec and effective exposure time of 15 sec. The line pairs were 3434·89 or 3396·85 for rhodium and 3408·13 for platinum. The pair (3396·85–3408·13) applies for the lower rhodium values. Although the lines lay in the rising area of the gamma curve they were sufficiently close together to permit a single density curve. With the technique employed the background in the neighbourhood of the lines was weak.

Koehler[33] used the spark and the interrupted arc for foil samples of platinum-rhodium alloys to be used as catalysers and for thermoelements. A technique was recorded for the estimation of some fourteen trace impurities, and included also is a list of the most sensitive undisturbed lines of silver, arsenic, gold, phosphorus, lead, antimony, silicon, tin and zinc.

For the determination of the platinum content of precious metal alloys, jewellers' scrap, etc., Manning and Coull[34] applied the Constant-Pair Method in which the added internal standard, molybdenum, at concentrations equal to platinum, provided lines of equal intensity for both metals. While no calibration curve was required, in the present author's opinion the laborious process of selecting the appropriate volumes of the standard molybdenum solution far outweighs the work involved in producing a working curve. As would be expected the accuracy of the method was not good; applied to a series of dental alloys the errors were about 15%.

Oberlander[35] recorded a list of suitable line pairs to be used for the determination of gold, palladium, rhodium, copper, iron, silver in platinum. For the determination of 0·00014–0·058% of gold and 0·0001–0·05% palladium in platinum wires, Ishitsuka[36] used the arc between carbon electrodes in one of which the wire was inlaid. Platinum was used as the internal standard. Gerlach and associates[37,38] discussed the precautions to be observed in the determination of impurities in platinum, iridium and rhodium. The most sensitive lines for the determination of the impurities were recorded. Homologous pairs of lines and their applications for the determination of iridium and rhodium in platinum are also included.

Stauss[39] discussed the use of the spectrograph in the platinum industry from the viewpoint of identification of alloys, special analyses for minor impurities and control of the purity of platinum and its alloys. In most instances the methods were essentially qualitative. The spectrographic control analysis for the platinum metals was also advocated by Pastore and Occhialini,[40,41] who wound wire samples around a copper rod and inserted the spirals between two carbon electrodes. Lines for the determination of platinum, gold and silver were recorded.

Babaeva and co-workers[42–45] have published a number of articles dealing with conventional spectroscopic determinations of small amounts of one or more platinum metals in precious metal alloys and salts. To determine small quantities of iridium and rhodium in complex platinum salts,[42] the authors used the direct current arc and carbon electrodes, the anode of which contained 2·5 mg to 3 mg of dried salt. Standards were prepared by evaporating solutions of suitable salts, and grinding the residue. Platinum lines were used as the internal standard. Because of the necessity of burning large samples and the fact that the accuracy attainable was only about 10–20%, the authors preferred activation by the spark method. The 3-mg sample was fastened to the carbon electrode by a drop of collodion and pressed in by grinding the carbon on a glass plate. The upper electrode was pointed. For concentrations of 0·5% to 0·05% iridium in platinum the lines 3220·79 for iridium and 3230·29 for platinum were used. Below 0·05% the platinum line was 3212·9. For rhodium the lines were 3396·8, or below 0·005%, 3434·9 with the platinum line 3427·92. The line pairs used were identical for either the bivalent or quadrivalent platinum and the working curves were consistent when one used the same compositions for the standard and unknown. The errors did not exceed 4·5% and the sensitivity was about 0·001%.

In a second paper[43] the authors recorded control methods for the determination of palladium in platinum, platinum in palladium and rhodium in iridium. The procedures contributed very little of value to spectrographic methods. A condensed spark and medium quartz spectrograph were used. The palladium in platinum varied from 10% to 0·001%; the platinum in palladium, from 5% to 0·001%; the rhodium in iridium, from 1% to 0·001%. The authors used the principal constituent for comparison and they recorded the most suitable lines for each of the three metals. They were unable to determine small proportions of iridium in rhodium. Standard solutions of pure platinum salts were evaporated, and the powder was added to graphite electrodes in two or more charges. For platinum and palladium determinations the mean error did not exceed 6·5%. For rhodium in iridium the mean error was 11%.

The authors also dealt with the determination of iridium, platinum, palladium in refined rhodium[44] and platinum and palladium in refined silver.[45]

For the determination of small quantities of iridium, platinum and rhodium in high purity palladium, Kheyfits[46] used both arc and spark with carbon electrodes, the upper and lower of which, subsequent to warming, were impregnated by adding aliquots of 0·01 ml of aqueous solutions.

The sensitivity of the spark method for platinum and iridium was 0·001% as compared to a range of 0·0005–0·02% for the AC arc. The accuracy ranged from ±3% to ±5%. In the case of the rhodium standards, which, of necessity, were prepared as sodium hexachlororhodate, the inaccuracy was increased due to the instability of the arc. However, in the presence of sodium salts the intensity of the palladium reference lines was increased. The authors used one of six palladium reference lines, lines 2929·79 or 2997·97 for platinum; 2924·79 or 3220·78 for iridium; and 3396·85 for rhodium.

X-RAY SPECTROSCOPIC METHODS

The applications of X-ray analytical methods to the platinum metals has been been the subject of only a few papers. In one of the earliest publications Schreiber[47] discussed techniques which would avoid the serious errors resulting from excessive heating of the anticathode. This is not a significant problem in modern X-ray methods which employ secondary or fluorescent emission. MacNevin and Hakkila[48,49] used the latter method for the determination of palladium, platinum, rhodium and iridium. These metals were applied as liquid solutions to heavy chromatographic paper and subsequently dried. This method avoided the variations in fluorescent energy caused by changes in tube-to-target distances. Calibration curves were constructed from known amounts of the metals plotted against the time required for 19,200 counts. In the case of mixtures there was some interference; K_α lines for palladium and rhodium were coincident, as were also the L_{α_2} for platinum and the L_{α_1} lines for iridium. To estimate the interference a correction curve, which indicated the counts per second attributed to the interfering element, was required. This method of ascertaining a correction factor becomes less valid as the proportion of the interfering metal is increased. To correct for instrument fluctuations, corrected counts per second were compared with the counts from a standard determined simultaneously rather than with a permanent calibration curve. This difficulty is analogous to that associated with intensity measurements of single lines in emission spectroscopy and constitutes one of the objectionable features of the fluorescent X-ray method. The error in positioning the sample, sample preparation, and counting for one standard deviation was found to be 1·86%.

Background corrections were required for each iridium determination and also for each palladium determination when the sample size exceeded 2 mg. The platinum background, assumed to be constant, was obtained by extrapolating the concentration–intensity curve to zero concentration.

The sensitivities, expressed as the mg per ml giving a count of 10% above background, was 0·10 for platinum, L_{β_1}; 0·20 for palladium, K_α; 0·14 for rhodium, K_α; and 0·02 for iridium, L_{α_1}.

The effect of foreign metals was discussed briefly. The enhancement and absorption of lines by associated base metal was assumed to be small because of the low concentrations of metals in the sample. The authors provided no experimental data dealing with interferences from line proximity of foreign elements.

POLAROGRAPHIC ANALYSIS OF PLATINUM METALS

Analytical literature contains no polarographic procedure for either the direct or indirect determination of platinum metals in ores, concentrates or complex alloys. Of the six platinum metals, potentially useful methods have been recorded for palladium, rhodium and osmium. None of the publications includes analytical data to indicate specific areas of application. The problems of interference from associated base metals are rarely discussed and, in general, little useful information is provided to indicate the effect of other platinum metals. Indeed the present author has found no polarographic report which deals with the questions of dissolution and subsequent preparation of the solutions to be analysed. Little of any immediate analytical value has been published for iridium. Most of the polarographic results are concerned with rhodium and with palladium. One cannot avoid the conclusion that there is here a fertile field of research. Polarographic methods will meet an analytical need in millimolar concentration ranges, and more important still, will provide some clarification concerning the character of dissolved species, of mixtures of valence states and, in general, useful descriptive data. Specifically, there could be value in polarographic methods applied to the various alloys obtained from fire assay processes. The advantages over classical methods of speed and simplicity could outweigh the greater accuracy of the former. Compared to spectrographic methods, applied to alloys when the maximum accuracy is required, the speed of polarographic methods may in some instances at least outweigh the labour involved in securing uniformity in solid electrodes.

Palladium

Willis[50] published a variety of potentially applicable polarographic methods for palladium. The work was almost entirely descriptive, with no attempt to provide procedural techniques nor analytical data. The most important problem of interferences from associated metals was not discussed. Obviously any forthcoming useful applications must await further researches. This author found a wave at —1·757 volts (SCE) for palladium^{II} dissolved in 0·1*M* potassium cyanide-*M* potassium chloride. The dissolved constituent $K_2[Pd(CN)_4]$ was reduced to palladium. In *M* ammonia-*M* ammonium chloride solutions of palladium^{II} tetra-ammino chloride, a well defined analytical step was obtained whose half-wave potential varied considerably with the palladium concentration. With *M* pyridine-*M* potassium chloride a step was produced which varied with the palladium concentration. The half-wave potential at $5 \times 10^{-3}M$ was —0·361 V, and at $2 \times 10^{-4}M$, it was —0·313 V. Under certain conditions ethylenediamine-potassium chloride solutions could also be used to produce an analytical step. With all of the above methods reduction involved a 2-electron change. The author concluded that the stability of the palladium amine complex increased with the basic strength of the co-ordinating amine; and with increased stability the reduction of the complex became less reversible. He correlated some interesting observations on the increase in negativity of the half-wave potential toward the base of each of the three groups of metals in column VIII of Mendelejeff's Table.

Wilson and Daniels[51] recorded a polarographic method for the determination of palladium following isolation by dimethylglyoxime. The authors compared their method favourably with the gravimetric methods which they incorrectly evaluate as "the most generally accepted methods now in use". The proposed procedure was applied to concentration ranges of 0·18 to 2·72 m-moles of palladium contained in ammonia-ammonium chloride buffer. A gelatin solution was used as a maximum suppressor. The diffusion currents corrected for residual current were measured at —1·10 volts (SCE). The precision ranged from 1% to 0·3% over a tenfold change in concentration; with concentrations of less than 0·35m-*M* there were greater deviations. Iridium, rhodium and platinum interfered. No results were included for osmium or ruthenium. Of the platinum metals examined only platinum^{IV} gave fairly reproducible waves. The presence of equimolar concentrations of silver, chromium, copper and nickel was permissible. With nickel as a contaminant the voltage was adjusted to —1·0 rather than —1·1. Gold, iron^{III} and titanium interfered seriously. This method will find very limited applications. The necessity for isolation by precipitation will encourage rejection in favour of various spectrophotometric methods.

Various authors have recorded procedures for the polarographic determination of palladium in the presence of gold and platinum. Linhart[52] recommended a solution of 0·1*N* lithium hydroxide in which the half-wave potential was —1·25 V. He proposed to use the method for the analysis of white gold, noting that cadmium interfered and must be removed, and for the determination of palladium and gold in platinum. No procedure was included and no analytical data were provided. Tomiček and co-workers[53] discussed the polarographic behaviour of palladium, gold and silver in various electrolytes. The three metals could be determined in the presence of each other. Bardin and Lyalikov[54] successfully used solid platinum electrodes in a supporting electrolyte of $0{\cdot}1N$ sodium nitrate to produce a clear-cut irreversible wave at 0·6–0·7 V. Since the polarographic process involved the deposition of palladium black on the platinum cathode an applied voltage which produced hydrogen was avoided. Dissolution of the latter resulted in a distorted polarogram which, at saturation, resulted in a current-voltage curve rising almost at zero. Regeneration of the cathode can be accomplished readily by treatment with hot nitric acid. In the absence of hydrogen, successive polarograms showed good agreement. To avoid the objectionable maximum the palladium solutions were treated with a small amount of hydrochloric acid. Within the concentration range studied there was a good analytical relationship between palladium content and wave length. The maximum error was 6% and the average error was 3%. The authors erroneously compare the results favourably with those to be obtained from gravimetric procedures. By applying a rotating electrode modification, results were obtained three to four times faster than with the stationary electrode and a greater sensitivity was attained, *e.g.*, 0·05 mg of palladium in 10 ml of solution (5 μg per ml). Polarographic and polarometric studies of noble metals were made by Beran and associates.[55] These authors examined the polarographic reactions of palladium, gold and some sixteen other elements in various mixtures of ethylenediamine tartrate and Complexones I, II and IV. The proposed procedure was recommended for dental alloys containing palladium and gold.

Platinum

Very few procedures have been proposed for the polarographic determination of platinum. English[56] devised a procedure for the determination of platinum in catalysts in which the metal is adsorbed on carbon. The procedure required a preliminary selective dissolution of base metals by hydrochloric acid containing titanium^{III} chloride. The organic residue containing carbon was oxidized and dissolved in *aqua regia*, and the solution was neutralized by sodium hydroxide with methyl red indicator and buffered with a mixture of citric acid and disodium phosphate. Gelatin was added and electrolysis was started at zero applied potential (SCE). The platinum^{IV} wave rose quickly to a well defined analytical level at about −0·6 V then dropped sharply to a second and lower plateau at −1·2 V. Since no starting horizontal was formed, the step height was taken as the vertical distance from the starting line to the intersection of the median line starting at the −0·3 V ordinate. The method involved standardisation difficulties arising from the instability of platinum^{IV} and resulting in errors as great as 6%. Reproducibility depended upon adherence to a prescribed procedure and could be maintained for a period of several hours. A further difficulty which could become serious in applications to complex platinum mixtures arises from the necessity of maintaining a prescribed volume of acid following dissolution processes. Larger volumes of acids increased the concentration of the supporting electrolyte which affected the step height. Further work will be necessary to extend the limited usefulness of this method, which has some potential value. Bardin and Lyalikov[57] determined platinum^{II} polarographically in a solution of $0{\cdot}1N$ sodium nitrate as the supporting electrolyte and with solid platinum electrodes. A platinum needle served as the cathode and a platinum plate as the anode. Oxygen interfered so much that the nitrogen, passed through for 45 minutes, was treated by copper to remove traces of oxygen. Two well-defined waves were produced at potentials of 0·7 V and 1·6 V. While within certain limits the effect of polarization was insignificant, the waves produced by a previously prepared platinum electrode coated with platinum black were appreciably distorted and less clearly defined. The results presented by the authors indicate a good analytical application for both waves. A modification of the equipment permitted polarographic determinations for platinum in concentrations of the order of 10^{-3} mg per ml.

In a second paper[58] the authors showed that the height of the second wave increased with increase in acidity and decreased with the addition of sodium hydroxide, from which it was concluded that the second wave was a hydrogen reduction wave. Because of this characteristic the second wave was not recommended for analytical application. On the other hand the height of the first wave, produced through the reduction of quadrivalent platinum to bivalent platinum was proportional to the platinum concentration and could be used analytically.

For proportions of platinum of less than $10^{-6}M$, Slendyk[59] used a catalytic hydrogen step at —1·0 V vs SCE from $2M$ hydrochloric acid solutions. While the analytical step was roughly proportional to the platinum concentration, neutral salts decreased the height of the plateau and this was accentuated with an increasing cation charge.

Rhodium

Willis[60] recorded a number of potentially useful polarographic methods for rhodium. Rhodium trichloride with excess of complexing reagent was used, the latter serving also as a supporting electrolyte. No analytical data were included. With M ammonium chloride a reversible two-electron analytical step was found at —0·928 V (SCE). The half-wave potential in $0{\cdot}02M$ ammonium chloride decreased to —0·799 V. In M ammonium chloride-M ammonium hydroxide a step occurred at —0·928 V, the height of which was proportional to a concentration range of $0{\cdot}5 \times 10^{-4}$ to $2{\cdot}5 \times 10^{-4}$ molar. With the chloropentammine rhodium complex in M potassium nitrate or potassium sulphate and gelatin, $E_{\frac{1}{2}}$ was —0·962 V and again a two-electron exchange was involved. With $3{\cdot}8 \times 10^{-4}M$ rhodium trichloride in thiocyanate solutions a step was obtained at —0·394 V. Zuman[61] used $0{\cdot}9M$ potassium thiocyanate solution and found a step with a half-wave potential of —0·43 volts vs SCE. In $0{\cdot}5M$ sodium fluoride there were two steps with half-wave potentials of —0·1 and —1·0 volts. For analytical work Willis[60] preferred a M pyridine-M potassium chloride medium. With concentrations of $3{\cdot}8 \times 10^{-4}M$ rhodium chloride solutions a step occurred at —0·414 V: the complex postulated was $K_3[RhPy_6]$ reduced to $K_2[RhPy_6]$. Repin[62,63] investigated the possible applications of a variety of complexing reagents for the polarographic determinations of rhodium and concluded that the only complexes of analytical use were formed with pyridine-hydrochloric acid added to produce a pH of 7. With ammonium hexachlororhodite a wave of reduction to divalent rhodium is formed. The wave becomes a peak and loses its analytical value in the presence of higher concentrations of pyridine or with rhodium concentrations greater than 40 mg per litre. At 1 mg of rhodium per litre the error may be as little as 2–4%. In the presence of platinum and iridium, rhodium can be determined by adding to the pyridine-hydrochloric solution of the ammonium salts of tervalent rhodium and quadrivalent iridium a few drops of sodium sulphite to produce bivalent platinum, whose proportions must not exceed 94% of the rhodium and platinum total. The rhodium wave was separated by 0·3 V from the catalytically depolarized hydrogen.

Osmium

While no complete polarographic method for the determination of osmium has been recorded some data of procedural value have been published. Crowell and co-workers[64] studied the character of the polarographic reduction of solutions of octovalent osmium oxide and of potassium osmate. Of various basic solutions, that in saturated lime water provided the most satisfactory polarographic waves. A dropping mercury cathode was used, with an anode of mercury covered with a thin layer of mercuric oxide in contact with lime water saturated with both calcium hydroxide and mercuric oxide. To avoid reduction of the osmium compound by mercury the two compartments were separated by a short arm with a stopcock. The potential of the half-cell at 25° was —0·091 volts vs NCE. With octovalent osmium oxide three steps appeared; the first representing a reduction to sexivalent osmium, the second to quadrivalent and the third to tervalent. The concentrations used varied between $1{\cdot}9 \times 10^{-4}M$ to $7{\cdot}1 \times 10^{-4}M$ OsO_4. With potassium osmate in lime water only two waves were evident, corresponding to the reduction of sexivalent and quadrivalent states. The half-wave potentials for these two reductions are respectively —0·44 volt and —1·20 volts vs NCE. No analytical results were provided, but the authors stated that by a direct comparison method with standard osmium solutions an accuracy of better than 5% could be attained. It is to be hoped that the method will be examined with a view to ascertaining its analytical value.

A polarographic method applicable to small amounts of osmium after isolation of the volatile oxide was proposed by Kolthoff and Parry.[65] The oxide in the presence of hydrogen peroxide, in an acetate buffered solution at pH 5, yields a kinetic or catalytic current whose maximum is measured at +0·23 volt vs SCE. Under the same conditions the rate of reduction of the octovalent oxide by the mercury pool anode was 2% a minute. The kinetic current was approximately linear in 8mM hydrogen peroxide over an osmium concentration range between $2M$ and $10 \times 10^{-7}M$. A calibration curve was recommended for analytical applications. The explanation for the catalytic current involved the reduction of the octovalent oxide to the sexivalent state and a rapid oxidation in the presence of hydrogen ions and hydrogen peroxide.

Ruthenium

The polarography of ruthenium in chloride-free perchloric acid was examined by Niedrach and Tevebaugh.[66] The authors postulated the existence in equilibrium of two distinct hydrolysed dissolved constituents of quadrivalent ruthenium. Due to the slow rate of change, two polarographic waves were found for the 1-electron reduction of these two species. In M perchloric acid the half wave potential of the first wave was +0·65 NHE; and for the second wave, +0·45 NHE. The reduction was irreversible. A third wave at —0·09 volts involved a reduction to bivalent ruthenium which could be re-oxidized slowly by perchloric acid to the quadrivalent form. The polarographic behaviour of ruthenium and of other platinum metals in acid solutions with a dropping mercury electrode was discussed by Slendyk and Herasymenko.[67] With ruthenium, catalytic hydrogen deposition occurred in three stages. In hydrochloric acid the deposition of hydrogen for various platinum metals, including ruthenium, compared with that for mercury at $-1{\cdot}17$ volts SCE, occurred over the following ranges: 0·5–0·6; 0·7–0·8; 0·9 volts, the exact values depending upon the pH and the concentrations of the platinum metals. This catalytic activity decreased from ruthenium to palladium, and from iridium to platinum. The authors explanation involved, in all cases, a reduction to metal and a type of alloy formation with mercury. The theory seems untenable in view of its dependence upon the existence of distinct stages in the character of alloy development. Aside from confirmation of the existence of multiple catalytic hydrogen stages this report has little or no analytical significance. Šušič[68] discussed the polarographic determination with the dropping mercury electrode of amounts of ruthenium of the order of 1×10^{-8} g to about 30×10^{-8} g in solutions of 0·9*M* perchloric acid, or EDTA, or EDTA together with ammonium acetate. With perchloric acid the single wave was a catalytic hydrogen wave and the ratios of concentration to the diffusion current showed a surprising precision. The EDTA with the same solutions of Ru^{III} and Ru^{IV} yielded three catalytic hydrogen waves, the highest of which was identical with the wave in the perchloric medium. The first wave had a half-wave potential of $-0{\cdot}88$ to $-0{\cdot}96$ V (SCE) between pH 1·06–2·3; the half-wave potential of the second wave under the same conditions varied from $-1{\cdot}16$ to $-1{\cdot}24$ V. With increasing pH the second wave was eliminated. The latter was recommended for determinations of quantities of ruthenium greater than 1×10^{-7} g per ml, with 0·001% gelatin and a pH $> 5{\cdot}4$ in either the EDTA or in EDTA with ammonium acetate as supporting electrolyte. Undoubtedly this polarographic method can be applied analytically, but further work and some modification will be required. The author provides no analytical procedure and, as in most polarographic papers, the methods of dissolution and of avoiding interference are not discussed.

Zusammenfassung—Ein kritischer Uberlick der Methoden zur spektrographischen und polarographischen Bestimmung der Platin-Metalle zum Juni 1958 wird angegeben.

Résumé—Cette mise au point concerne les publications appropriées examinées jusqu'en juin 1958. Les méthodes ont été jugées du point de vue de leurs applications analytiques aux essais de perle, aux précipités de platine métallique et aux alliages des métaux de la mine du platine avec ou sans impuretés des métaux principaux.

Aucune méthode spectrographique n'a été signalée pour le dosage direct des métaux de la mine du platine dans les minerais et les concentrès. Pour le dosage du palladium, du platine et du rhodium dans le minerais et les concentrès, les méthodes spectrographiques les plus exactes nécessitent une extraction préliminaire par voie sèche pour obtenir un culot de plomb ou une perle d'argent. Pour ces derniers, pour d'autres alliages, pour des précipités, etc..., les méthodes les plus exactes impliquent des traitements spéciaux pour obtenir une composition uniforme et réaliser des étalons ayant des passés métallurgiques identiques. Aucune méthode spectrographique satisfaisante n'a été signalée pour le dosage direct ou indirect de l'iridium du ruthenium et de l'osmium dans les minerais, les concentrès ou les alliages complexes.

Aucune des fréquentes affirmations selon lesquelles les méthodes spectrographiques fourniraient une plus grande exactitude que les méthodes par voie humide, n'a été confirmées et elles sont toutes inacceptables. Les quelques données existantes montrent qu'avec un analyste compétent et dans les meilleures conditions l'exactitude des deux méthodes est du même ordre.

Pour l'examen qualitatif des impuretés d'un précipité etc. contenant des traces de nombreux métaux, la méthode spectrographique est nettement supérieure aux méthodes par voie humide.

Pour les métaux de la mine du platine les méthodes polarographiques ne concernent que des mélanges à peu de constituants. Aucun procédé n'a été signalé permettant leur application satisfaisante aux essais de perles ou de culots. Peu de procédés détaillés ont été signalés pour le dosage de chaque métal de la mine du platine et aucune méthode ne comporte les procédés usuels permettant la dissolution d'un système à constituants multiples. Les méthodes polarographiques peuvent être, sans aucun doute, d'utiles rivales dans les domaines de concentrations en dessous desquelles les méthodes classiques ne sont plus applicables. De plus les deux méthodes spectrographiques et polarographiques possèdent le grand avantage de la rapidité lorsqu'il s'agit d'un grand nombre d'échantillons de compositions voisines.

Trop peu de méthodes par spectrographie aux rayons X ont été signalées pour juger leur présision.

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ANALYTICAL APPLICATIONS OF XYLENOL ORANGE—II

SPECTROPHOTOMETRIC STUDY ON THE ZIRCONIUM-XYLENOL ORANGE COMPLEX

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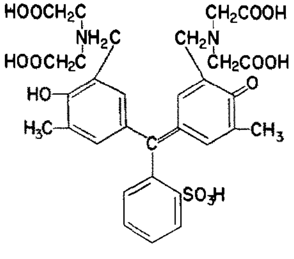
(*Received* 17 *January* 1959)

Summary—The purplish-red complex formed from zirconium and Xylenol Orange has been studied by spectrophotometric methods and shown to contain zirconium and reagent in the ratio 1 : 1. The formation constant of this complex has been measured as 4.0×10^7.

IN Part I of this series,[1] Xylenol Orange has been proven to be a sensitive and highly selective reagent for zirconium (and hafnium), and its use in the determination of small amounts of zirconium in high temperature alloys has been described elsewhere[2]. This paper presents the results of a spectrophotometric study on the zirconium-Xylenol Orange complex.

Xylenol Orange, which has the following structure, is an analogue of EDTA and therefore would be expected to form a 1 : 1 complex.



Xylenol Orange

EXPERIMENTAL

Reagents

Xylenol Orange solution: 0.065 g of the sodium salt (as supplied by CHEMAPOL) was dissolved in water and diluted to 1 litre. This gave a $1 \times 10^{-7}M$ solution.

Zirconium solution: A $2 \times 10^{-7}M$ solution was prepared from zirconium tetrachloride in $0.8N$ perchloric acid and standardized by EDTA.[3]

Absorption measurements were made with a Beckman Spectrophotometer, Model DU using 1-cm silica cells.

THE ZIRCONIUM-XYLENOL ORANGE COMPLEX

The spectra of Xylenol Orange and its zirconium complex in $0.8N$ perchloric acid medium have been determined.[1] The complex has a maximum absorption at 535 mμ.

The mole ratio of the zirconium-Xylenol Orange complex was investigated by the mole ratio method and Job's method.[4] In the mole ratio method, 9.5×10^{-7} mole of zirconium were mixed with various amounts of Xylenol Orange ($1 \times 10^{-7}M$

solution) in approximately 0.8*N* perchloric acid. The total volume was 50 ml. The solution was set aside for more than 30 minutes before making the absorbance measurement using water as blank (see Fig. 1). In Job's method, mixtures of varying proportions of equimolecular solutions of zirconium and Xylenol Orange were prepared, keeping the total volume at 50 ml, and their absorbances were measured at 535 mμ. The data are plotted against the composition of the mixtures (Fig. 2). Since Xylenol Orange solution absorbs slightly at 535 mμ, a correction was made. Both methods indicate that a 1 : 1 complex was formed under the conditions investigated.

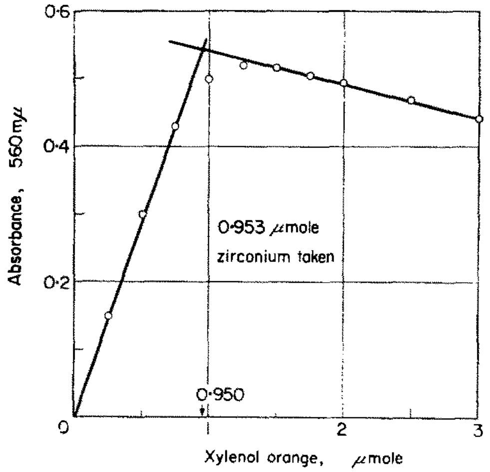


FIG. 1.

FORMATION CONSTANT OF THE ZIRCONIUM-XYLENOL ORANGE COMPLEX

The formation constant of the complex has been calculated from Fig. 2 by the method similarly used for a similar purpose by Majumdar and Chakrabartty.[5] The formation is in accordance with the following equation

$$Zr + XO \rightleftharpoons ZrXO$$

where XO represents the molecule of Xylenol Orange.

Hence
$$K = \frac{[ZrXO]}{[Zr]\cdot[XO]} \quad \text{or} \quad \frac{[x]}{[a-x]\,[b-x]} \qquad (1)$$

The concentrations of free zirconium and Xylenol Orange in the solution can be found if the concentration of the zirconium Xylenol Orange formed [*x*], the total concentration of zirconium [*a*] and the total concentration of Xylenol Orange [*b*] are known. By drawing a line to intersect curves I_c and II_c at A and B, where solutions A and B have the same concentration of Zirconium-Xylenol Orange complex, [*x*] can be calculated from the following relation:

$$K\ (\text{formation constant}) = \frac{[x_1]}{[a_1 - x_1]\,[b_1 - x_1]} = \frac{[x_2]}{[a_2 - x_2]\,[b_2 - x_2]}$$

Since $[x_1] = [x_2]$ we obtain,

$$[x] = \frac{[a_1 b_1 - a_2 b_2]}{[a_1 + b_1] - [a_2 + b_2]} \tag{2}$$

The concentrations of zirconium $[a_1]$ and Xylenol Orange $[b_1]$ used in solution A and those of zirconium $[a_2]$ and Xylenol Orange $[b_2]$ used in solution B can be easily found at points A_1 and B_1 from Fig. 2. The formation constant K is then calculated from equation (1). This is a very convenient way of measuring the formation constant of a coloured complex with the mole ratio 1 : 1.

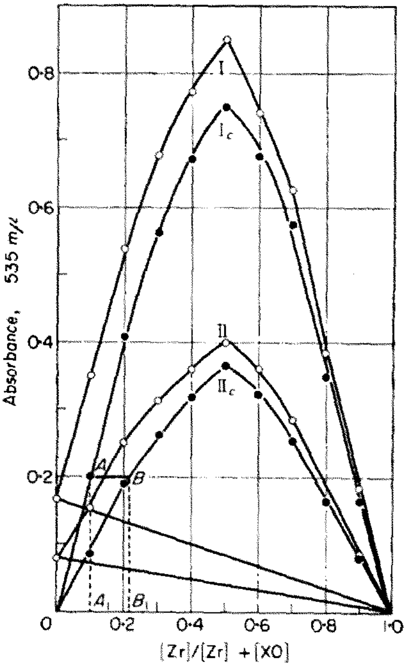


Fig. 2.

Application of this method gave a value of $K = 4.0 \times 10^7$. This value is not high as compared with that of the stability constant for the zirconium-EDTA complex ($10^{19.9}$). Therefore Xylenol Orange can serve as a metal indicator in the EDTA titration of zirconium, and its zirconium complex is easily masked by other strong complexing agents such as EDTA, fluoride, phosphate, oxalate, and large amounts of sulphate.

Zusammenfassung—Es wurde der purpurrote Zirkon Xylenol Orange Komplex auf spectrophotometrischem Wege untersucht. Das Verhältnis von Zirkon und Reagens betrug 1 : 1. Die Bildungskonstante dieses Komplexes wurde als 4.0×10^7 bestimmt.

Résumé—Le complexe rouge-pourpre du Zirconium avec le Xylenol Orange a été étudié par Spectrophotométrie. On a montré qu'il contient le Zirconium et le réactif dans le rapport 1 : 1. La constante de formation de ce complexe a été mesurée, et est égale à $4{,}0 \times 10^7$.

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SPECTROPHOTOMETRIC DETERMINATION OF RUTHENIUM WITH N:N'-BIS-(3-DIMETHYL-AMINOPROPYL)DITHIO-OXAMIDE*

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Summary—N:N'-Bis-(3-dimethylaminopropyl)dithio-oxamide, a derivative of rubeanic acid, reacts with ruthenium in a strong hydrochloric acid solution to give a soluble blue complex which has been made the basis for the determination of trace quantities of the element. Optimum conditions for the use of the reagent have been studied. Well-known distillation techniques have been successfully applied to quantities of ruthenium ranging from 14.8 μg to 177.9 μg. The sensitivity is 0.020 $\mu g/cm^2$.

INTRODUCTION

SEVERAL investigations have been carried out in recent years on the spectrophotometric determination of ruthenium. Ayres and Young[1,2] have studied thiourea and dithio-oxamide (rubeanic acid), and DeFord[3] thiourea, as colorimetric reagents for this metal. Currah, Fischel, McBryde and Beamish[4] investigated the reaction between ruthenium and *p*-nitrosodimethylaniline. Breckenridge and Singer[5] studied the ruthenium-5-hydroxyquinoline-8-carboxylic acid system. Recently Steele and Yoe[6] have proposed 1-napthylamine-3:5:7-trisulphonic acid for the determination of ruthenium.

In this paper N:N'-bis-(3-dimethylaminopropyl)dithio-oxamide is recommended as a reagent for the spectrophotometric determination of ruthenium. This compound has recently been applied by Jacobs and Yoe[7] to the simultaneous spectrophotometric determination of cobalt, nickel and copper. The latter reactions are carried out at pH 9 with immediate development of colour at room temperature. The reaction with ruthenium requires heat in the presence of high concentrations of hydrochloric acid.

EXPERIMENTAL

Apparatus

Spectrophotometers: Beckman spectrophotometers, Model DK-2 and Model DU, with 1-cm matched Corex cells were used for all absorbance measurements.

Distillation apparatus: The still used for the distillation of ruthenium was the same as the one proposed by Steele and Yoe.[8]

Reagents

Standard ruthenium solution: Approximately 0.4 g of ruthenium chloride was dissolved in distilled water. Concentrated hydrochloric acid was added to give a final concentration of one molar in 500 ml. The solution was standardized gravimetrically by precipitating the ruthenium as the hydrated oxide, igniting in air and then in hydrogen to the metal. The solution contained 0.593 mg of ruthenium per ml. More dilute solutions were prepared as needed.

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Reagent solution. A 3 × $10^{-3}M$ solution of N:N′-bis-(3-dimethylaminopropyl)dithio-oxamide was prepared by dissolving 87 mg of the compound in 100 ml of 95 % ethanol.

Other reagents: All other reagents were analytical grade and were used without further purification.

Absorbance curves

Fig. 1 shows absorbance curves of the reagent (1.8 × $10^{-4}M$) and the ruthenium complex (3.56 ppm). The hydrochloric acid concentration in both solutions was approximately 7.5*M*. The solutions were heated in a boiling-water bath for 15 minutes. The ruthenium complex has a maximum absorbance at 630 mμ. The reagent does not absorb above 400 mμ, so distilled water was used as a reference.

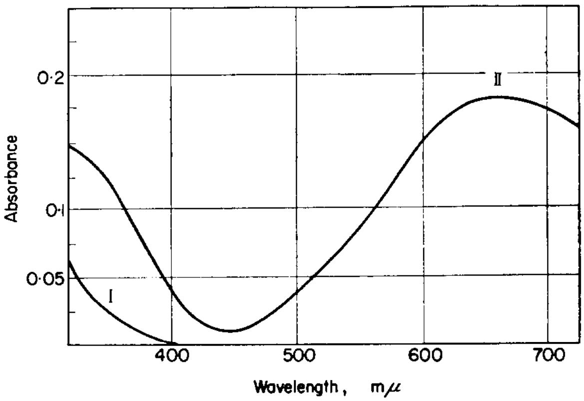

FIG. 1. Absorbance curves for reagent (I) and its ruthenium complex (II).

Effect of molarity of hydrochloric acid

Table I illustrates the effect of the concentration of hydrochloric acid on the intensity of the colour reaction. The absorbance of the complex was found to increase up to a concentration of hydrochloric acid corresponding to approximately 7.5*M*.

TABLE I. EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID ON ABSORBANCE OF RUTHENIUM COMPLEX (3.56 ppm of Ru)

Molarity of HCl	A_s at 630 mμ
0.80	0.115
1.6	0.141
2.4	0.150
3.2	0.157
4.0	0.165
6.4	0.170
7.5	0.179
8.6	0.180

Effect of time of heating

Maximum colour development was reached after heating 15 ml of the sample in a boiling water bath for 15 minutes. The 15 ml of solution contained 3 ml of the reagent solution (3 × $10^{-3}M$) and

10 ml of concentrated hydrochloric acid along with the desired quantity of Ru^{III}. After this heating period the solution was cooled and diluted to 25 ml with distilled water. It is necessary to use about a 10-fold excess of reagent in order to assure complete colour development.

Conformity to Beer's law

Beer's law was found to be obeyed by the complex over the range investigated, 0.27 ppm to 9.52 ppm ruthenium.

Effect of diverse ions

It was found that concentrations of Rh^{III} and Ir^{IV} comparable to the amount of Ru^{III} present hindered the development of the ruthenium complex. It appears that these ions form colourless complexes with the reagent. No colour could be developed with the ruthenium in the presence of these two ions even when three times the normal amount of reagent solution was used. Pt^{IV} forms a rose colour with the reagent *when heated*, but not in the cold. This is probably due to a Pt^{II} complex resulting from the reduction of Pt^{IV} to Pt^{II} upon heating with excess reagent. Platinum interferes with the development of the ruthenium complex when present in amounts equivalent to the amount of ruthenium present. A bright yellow complex is formed when Pd^{II} reacts with the reagent in strong hydrochloric acid. This reaction takes place at room temperature. It offers promise of being a good reaction for palladium and is currently being investigated. Palladium can be tolerated as long as its concentration is no more than twice that of the ruthenium present. Osmium, as the osmate ion, forms a complex with the reagent whose colour changes from a green to red and finally to brown. The nature of the final product is such that it is difficult to characterize spectrally.

These studies indicate the advisibility of a prior separation of the ruthenium. This is accomplished by distillation of the ruthenium as ruthenium tetroxide.

Distillation of ruthenium

The apparatus employed for the distillation of ruthenium is the same as the one reported by Steele and Yoe.[8] In our work only the first receiver is used, since osmium is removed in a prior treatment. If osmium is present, the sample is heated with 6*M* nitric acid *in a hood* for 15 minutes, thereby converting the osmium to the volatile osmium tetroxide.

Recommended distillation procedure: If the sample contains chlorides, it must be heated with sulphuric acid to fumes of sulphur trioxide to remove chlorides, since their presence hinders the volatilization of ruthenium tetroxide. Place the sample in a 200-ml flask and dilute to about 25 ml with distilled water. Add concentrated sulphuric acid to give a final concentration of about 10% by weight. Add twenty-five ml of a 10% (by weight) solution of sodium bromate and distil the sample for 15 minutes. Collect the ruthenium tetroxide in 10 ml of 6*M* hydrochloric acid and carry through the procedure for analysis.

Procedure for analysis

Evaporate the distillate containing the ruthenium tetroxide to about 1 ml and then wash into a 25-ml volumetric flask with 1 or 2 ml of distilled water. Then add 10 ml of concentrated hydrochloric acid and 3 ml of the reagent solution. Head the sample in a boiling water bath for 15 minutes, cool, and dilute to the mark with distilled water. Measure the absorbance of the solution at 630 mμ against a distilled water blank. Then determine the concentration of ruthenium from a calibration curve.

Analysis of synthetic samples

Synthetic samples containing ruthenium alone and in the presence of other platinum metals were carried through the distillation procedure and then analysed by the recommended procedure. The results are given in Table II.

TABLE II. ANALYSIS OF SYNTHETIC SAMPLES

Sample	μg Ru added	μg Ru found	% Recovery
1	59.4	62.5	105
2	29.7	31.3	105
3	14.8	13.3	90
4	89.1	85.5	96
5	59.4	60.5	102
6	118.6	117.5	99
7	29.7	28.8	97
8	117.9	177.5	100
9*	29.7	27.3	93
10*	59.4	60.5	102
11*	89.1	87.5	98

* Os, 250: Pd, 1000; Pt, 1000; Ir, 1000; Rh, 1000.

Sensitivity

The sensitivity of the colour reaction as defined by Sandell[9] is 0.020 $\mu g/cm^2$.

Standard deviation

The standard deviation was based upon ten samples which contained 89.1 micrograms of ruthenium. Each sample was carried through the distillation procedure and analysed according to the recommended procedure. The standard deviation was 0.003 absorbance unit or 0.06 ppm ruthenium.

CONCLUSIONS

The proposed reagent has the advantage over rubeanic acid and thiourea in that the ruthenium complex is much more soluble than the complexes of these two compounds. The time of heating is about one-half that of the rubeanic acid and thiourea systems. The sensitivity of the new colour reaction is less than that claimed by Ayres and Young for rubeanic acid. In our hands, however, the sensitivity claimed for rubeanic acid was not obtained, perhaps through inexperience with the method. The sensitivity of the new reagent is slightly greater than the ruthenium–thiourea reaction.

p-Nitrosodimethylaniline is more sensitive than the new reagent but here again the new complex is more soluble and maximum intensity is reached in 15 minutes, whereas the ruthenium complex with *p*-nitrosodimethylaniline requires 50 minutes for maximum colour development.

N:N′-bis-(3-dimethylaminopropyl)dithio-oxamide should be a valuable reagent for the determination of trace quantities of ruthenium. The procedure is more rapid and the accuracy compares favorably with existing methods.

Acknowledgement—The authors wish to express their thanks to the Mallinckrodt Chemical Works for their gift of the N:N′-bis-(3-dimethylaminopropyl)dithio-oxamide used in this work.

Zusammenfassung—Zur Bestimmung von Rutheniumspuren wird der lösliche blaue Komplex, der mit N,N′-bis(3-dimethylaminopropyl)dithio-Oxamid (ein Derivat der Rubeanwasserstoffsäure) in stark salzsaurer Lösung entsteht, herangezogen. Die besten Arbeitsbedingungen wurden studiert und bekannte Destillationsverfahren bei Rutheniummengen von 14,8–177,9 μg angewendet. Die Empfindlichkeit beträgt 0,020 $\mu g/cm^2$.

Résumé—La N-N′-bis-(3-diméthylamino propyl)dithio-oxamide, dérivé de l'acide rubéanique, réagit avec le ruthénium en solution acide chlorhydrique fort pour donner un complexe bleu soluble qui est à la base du dosage de traces de cet élément. Les auteurs ont étudié les meilleures conditions d'utilisation de ce réactif. Ils ont appliqué avec succès des techniques de distillation bien connues à des quantités de ruthenium allant de 14,8 μg à 177,9 μg. La sensibilité est 0,020 μg/cm^2.

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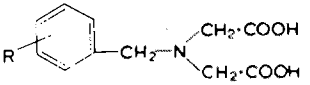
PRELIMINARY COMMUNICATIONS

New chelons based on pyridine

(*Received* 20 *October* 1958)

SELECTIVITY in chelometric titration has been achieved principally through applying selective metallochromic indicators, masking or demasking agents, and selective titrants. Within the last few years numerous metallochromic indicators have been synthesized and studied for their applicability in chelometric titrations and these have been recently reviewed by Barnard, Broad, Flaschka.[1] The unique properties of certain of these indicators have widened the scope of metal ion analysis with EDTA tremendously and undoubtedly more studies of this nature will be forthcoming. Recently the proposal of new chelons suitable for selective titration has brought increased attention. Aside from the classical EDTA the chelons triethylenetetramine (trien), tetraethylenepentamine (tetren), and ethylene glycol-*bis*(β-aminoethyl ether)-N:N′-tetra-acetic acid (EGTA)[3-7] have been proposed as titrants because of some unique behaviour which allows them to be employed as selective titrants. For example EGTA complexes calcium ($\log K = 11$) much more tightly than magnesium ($\log K = 5.2$) and thereby permits selective titrations of the former.[6,7] Polyamines, such as trien and tetren, form stable complexes with a fairly restricted group of metal ions (namely the later transition metals) and may be utilized for the titration of these particular metals in the presence of alkaline earths, the rare earths and heavy metals.

In this laboratory a number of new chelons based upon pyridine have recently been synthesized and are under current investigations. These may be designated as derivatives of 2-aminomethyl pyridine-N-N-diacetic acid (abbreviated PADA).



Where R corresponds to —H, $—SO_3^-$, $—COO^-$, $—CH_3$, or $—CH_2—N(CH_2COOH)_2$. This paper represents the preliminary report of some of the unusual properties of the 6-methyl derivative.

Unlike EDTA, the 6-methyl PADA does not form stable complexes with the alkaline earths and rare earths, but is otherwise similar. Unlike the polyamines, 6-methyl PADA reacts with lead and bismuth in acid solution. Thus by judicious choice of chelons and the proper use of the pH effect, selective titrations can be achieved with rather complicated mixtures of metal ions.

Potentiometric detection of end-points was chosen for this study because of the rather specific activity of this type of end-point detection; in other words, non-titrated metals which may block the action of metallochromic indicators do not block the detection of end-points with the mercury electrode. Also the mercury electrode is applicable over almost the entire pH range and thus selectivity by the pH effect is readily obtained. Some of the results are illustrated in Fig. 1 for titrations with 6-methyl PADA. Studies are now under way to determine the stability constants for these chelons with a representative group of metal ions and this work will be reported in detail later.

EXPERIMENTAL

Potentiometric end-point

The electrode system consisted of a mercury indicator electrode and a calomel reference electrode;[8] the potential being followed by means of Leeds and Northrop pH meter (Cat. No. 7664). In the titration of every ion except mercury,^{II} a drop of 10^{-3} *M* mercury^{II}-chelonate is added to establish a reasonably meaningful potential.[8]

Reagent and solutions

6-methyl PADA standard solutions. 3.144 grams of the solid dipotassium dry salt was dissolved in demineralized water and diluted to 100 ml to prepare $0.1M$ solution.

Metal salt solutions: These were prepared by weighing the approximate amounts of salts (using high purity chemicals) to prepare $0.01M$ solutions and standardized against EDTA solution.

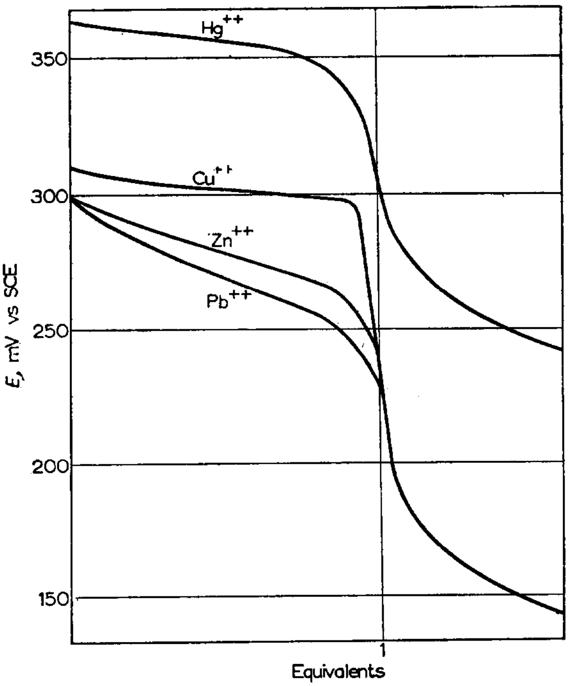


FIG. 1. Titration curves with 6-methyl PADA using mercury electrode. Acetate buffer (pH 5.5). Alkaline earths, rare earths, scandium, yttrium, aluminium do not interfere.

Buffers: Ammonia, triethanolamine and acetate buffers were prepared by mixing one mole of base and of nitric acid and diluting to 1 litre. These were stored in polyethylene bottles.

Mercury^{II}-chelonate: $0.001M$ prepared by mixing 10 ml of $0.002M$ mercuric nitrate with an equivalent amount of *6-methyl PADA* and neutralizing with sodium hydroxide to pH 7.0.

PROCEDURE

The titrations of different metal ions were carried out in 50 ml titration cell equipped with a magnetic stirrer and a glass electrode to check the pH during the titration. Samples containing $10^{-3}M$ metal ion and at most $10^{-2}M$ buffer and 1 drop $10^{-3}M$ mercury^{II}-chelonate were titrated with $0.1M$ solution of the chelon from a Gilmont microburette (total displacement 1 ml, subdivided into 0.0002 ml).

RESULTS

Fig. 1 shows the potentiometric curve of different metal ions titrated with 6-methyl PADA in acetate buffer at pH 5.5. Rare earths and alkaline earths are not titrated and do not interfere at this pH. The direct titrations of copper, cobalt, nickel, zinc and lead in ammonia buffer (pH 9.5) were feasible with fairly sharp breaks. Calcium, strontium, and barium do not titrate at this or higher pH. Bismuth at pH 1.5 as well as mercury^{II} nitrates could be titrated in nitric acid.

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Metalfluorechromic indicators

(*Received* 23 *January* 1959)

As a result of the examination of sixteen metalfluorechromic indicators, it has become apparent that metal ions are capable of forming two kinds of complexes with these indicators.

The "normal complex" is demonstrated by the quenching of the fluorescence of calcein W by copper ions.[1] In this instance the free indicator exists in a form H_nI^{n-6} which fluoresces. The formation of the copper complex results in the quenching of the fluorescence and must be interpreted as bringing about the electronic configuration found in the indicator anion I^{-6}. This type of reaction would be expected with metalfluorechromic indicators since an analogous phenomenon takes place with metallochromic indicators. That is the formation of a metal complex with a metallochromic indicator results in the appearance of the "alkaline colour" of the free indicator at a pH at which an "acid colour" would normally exist. With the metalfluorechromic indicators studied to date, copper, manganese, nickel, cobalt and palladium are capable of forming the 'normal complex' at appropriate pH values.

A second type of reaction which I prefer to call an "indicator reversal complex" is also demonstrated by calcein W. This is used in the titration of calcium with EDTA.[2] In this case the free indicator at a high pH exists in the form I^{-6}, which does not fluoresce. The addition of calcium causes the fluorescence to appear even though the pH of the solution is so high that the free indicator does not fluoresce. This phenomenon must be interpreted as an indication that calcium brings about the electronic configuration of a fluorescing anion H_nI^{n-6} presumbly in the form CaH_nI^{n-4}. In addition to calcium, barium, strontium, mercury, zinc, lead and others react in this manner.

In no case has an element been found which will take part in both types of complex formation.

A mechanism for this phenomenon may be suggested in the possibility of the formation of two geometrically different chelates at the fluorechromic site. These two configurations are illustrated in Fig. 1.

Fig. 1a illustrates the normal complex which results in the quenching of the fluorescence of the free indicator. The copper ion is attached to the phenolic oxygen and thus alters the part which this portion of the molecule can contribute to fluorescence.

Fig. 1b illustrates a second configuration which can exist with this functional group. In this instance the metal ions (Ca, Sr, Ba, Hg, etc.) do not chelate in a manner which binds the phenolic oxygen. This explains why these elements do not quench the fluorescence of the free indicator. The enhancement of the fluorescence by the metal ions which form "an indicator reversal complex" also may be explained by this mechanism. Function groups of this type form complexes of the type MHL. In addition it is not unusual for log K^M_{MHL} and log K^M_{ML} to differ by only a single order of

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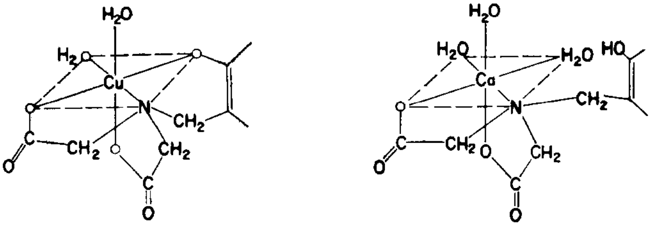

(a) (b)

FIG. 1.

The phenomenon which has been referred to as a "blocking reaction" with metallochromic indicators[5] can be explained by the same mechanism.

This phenomenon is being examined in considerable detail and will be reported on at a later date.

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Rapid method for coulometric analysis using an I-Q recorder

(*Received* 19 *March* 1959)

A RAPID method which employs an I-Q recorder has been developed for controlled potential coulometric analysis. This I-Q recorder uses the bevel gear differential as main mechanism. The recorder shows the electrolysis current, i, along the Y-axis and the quantity of electricity, Q, (the integrated value of the electrolysis current, i) along the X-axis. This is unlike most recorders which show time t along the X-axis. The current integration is performed by the differential gear, a tachogenerator to stabilize, and various motors.[1] This integrating mechanism derives a chart instead of the counter used in the direct-reading current integrator. Integration of current from the neighborhood of zero percent of rated current is possible; also background current is mechanically cancelled from the total electrolysis current which passes from the cell. The value of Q on the chart is the net electrolysis current. The background current is assumed to be always constant.[2]

In coulometric analysis with controlled potential,

$$i_t = i_0\, 10^{-Kt} \tag{1}$$

and

$$Q = \int_0^t i_t \, dt \tag{2}$$

where i_0 = initial current at zero time.
i_t = current at time t.
K = constant.
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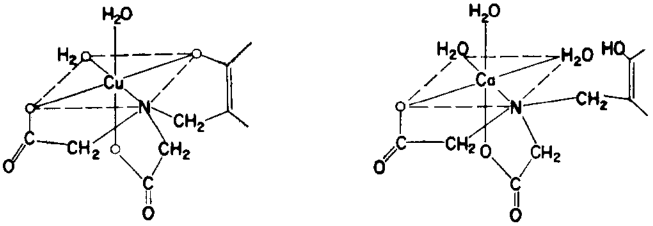

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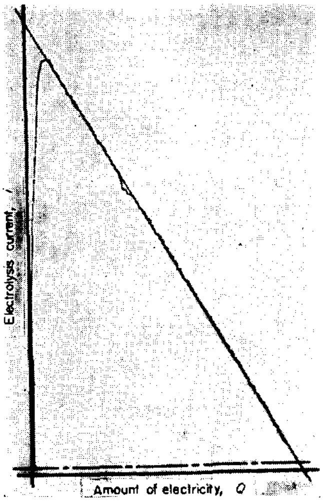

FIG. 1

From equations (1) and (2) it is found[3] that

$$Q = \frac{i_0 - i_t}{2.303\ \mathrm{K}} \tag{3}$$

The current plotted against the quantity of electricity shows that the relation is effectively a straight line. Therefore measurement of the electrolysis current for only the initial few minutes is sufficient, since the current is large and the recording distance of Q is greatest at this time. The inclination of the entire curve is determined by extending a line from this recorded section. By extrapolation, the estimated resultant quantity of electricity is found at the intersection with the X-axis.

The experimental determination of semimicro amounts of copper has confirmed the relation shown in equation (3). Fig. 1 shows the chart obtained in the determination of 0.5 mg of copper.

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SHORT COMMUNICATION

The heterolytic and homolytic dissociation of bromine chloride and determination of the bromine formed during homolytic dissociation

(*Received* 9 *February* 1959)

WHILE developing the iodometric method for the determination of bromide ions already reported[1] and in further experiments, the chemical behaviour of bromine chloride was subjected to a thorough investigation. We observed[2] that, in the molecule of bromine chloride, bromine possesses a $+\delta$ charge whilst chlorine has a $-\delta$ charge. Accordingly, bromine chloride dissociates in aqueous solution to bromine ions of positive δ charge and to chloride ions of negative δ charge. Applying this assumption, all the reactions of bromine chloride studied by us could be interpreted, in general, with success. However, we were unable to explain the phenomenon then mentioned[3] that when stoichiometric bromine chloride, *i.e.* containing equivalent amounts of bromine and chlorine, reacted in aqueous solution with excess cyanide, and the bromine cyanide formed was measured by iodometry, it was found that only 97–98 % of bromine chloride was converted into bromine cyanide. A similar observation was reported by L. Molnár.[4] In the presence of excess chlorine, bromine chloride quantitatively yielded bromine cyanide.

In the course of the investigation of the standard bromine chloride solution, a method was also evolved for the determination of the content of elementary bromine in the aqueous solution of bromine chloride. This method, which is given in detail below, essentially consists in treating the solution with excess hydrogen cyanide, when bromine chloride is converted into bromine cyanide and chloride ions whilst elementary bromine yields bromine cyanide and bromide ions. Bromine cyanide and excess hydrogen cyanide are then removed from the solution by an inert gas (CO_2) or by cautiously boiling the boric acid solution. The residual bromide ions, the amount of which is equivalent to the original content of elementary bromine, are determined by the bromine cyanide method[1] already mentioned.

By this method, we investigated solutions of bromine chloride prepared from equivalent amounts of bromine and chlorine and other solutions of bromine chloride containing different quantities of elementary chlorine and elementary bromine. No elementary bromine was found in solutions of bromine chloride prepared with excess chlorine. However, in solutions prepared from equivalent amounts of chlorine and bromine we found, on removal of excess hydrogen cyanide and bromine cyanide formed during the cyanide reaction, a quantity of bromide just equal to the deficiency in the reaction between bromine chloride and cyanide already mentioned. In solutions of bromine chloride prepared by excess bromine we obtained, within the limits of experimental errors, the quantity of bromine which was in excess. The deficiency of bromine found in investigating stoichiometric bromine chloride apparently did not now occur.

From this phenomenon we concluded that, in addition to the heterolytic dissociation (to Br^+ and Cl^-) characteristic of bromine chloride in aqueous solution, there must also be a homolytic dissociation (to Br_2 and Cl_2) to a small extent.* This is ascribed to the relatively small difference in the electron affinities of bromine and chlorine. This dissociation is suppressed by the presence of elementary chlorine or bromine. Recently, we described[6] a similar phenomenon in connection with iodine bromide. The reaction of stoichiometric bromine chloride and cyanide is due to the homolytic dissociation which takes place to a small extent. The bromine liberated during homolytic dissociation reacts with cyanide ions, and affords bromine cyanide and bromide ions.

As already mentioned elsewhere, these parallel dissociations make the analytical application of iodine bromide difficult. The elementary bromine liberated during the homolytic dissociation of iodine bromide reacts with aromatic compounds at a rate higher than that of iodine of bond (oxidation) number +1 which forms during heterolytic dissociation.[7] Accordingly, iodine bromide has partly an

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* It is known[5] that in solvents of low dielectric constant the homolytic dissociation of interhaloid compounds predominates whilst solvents of high dielectric constant, such as water, encourage heterolytic dissociation.

TABLE 1.—DETERMINATION OF THE CONTENT OF ELEMENTARY BROMINE IS SOLUTIONS OF BROMINE CHLORIDE

Number	Composition of the solution, *ml*			Br_2 found, *ml* of $0{\cdot}01N$ Br_2 solution	Deviation		Bromine formed during homolytic dissociation %
	$0{\cdot}1N$ aqueous solution of bromine chloride	$0{\cdot}1N$ Br_2-water	$0{\cdot}1N$ Cl_2- water		*ml* of $0{\cdot}01N$ Br_2 solution	%	
1	10·00	—	—	1·80	—	—	1·80
2	10·00	—	—	2·20	—	—	2·2
3	10·00	—	5·00	0·00	—	—	—
4	10·00	—	1·00	0·05	—	—	—
5	10·00	1·00	—	10·08	+0·08 ($0{\cdot}1N$ Br_2-solution)	+0·8	—
6	10·00	5·00	—	4·95	−0·05	−1·0	—
7	10·00	10·00	—	10·12	+0·12	+0·2	—

iodinating and partly a brominating effect. (In an aqueous solution, under certain conditions, the iodinating effect can be raised to 90–94% or even to 100%).

However, the two different types of dissociation of bromine chloride do not interfere with the analytical application of this reagent. Bromine of bond (oxidation) number +1 which forms during the predominant heterolytic dissociation reacts with aromatic compounds at a rate appreciably higher than that of elementary bromine liberated during homolytic dissociation and particularly than that of chlorine. Thus, bromine chloride in aqueous solution behaves in its aromatic substitution reactions as a brominating agent. Therefore, it is possible to use a standard solution of bromine chloride analytically with success.[3]

DETERMINATION OF FREE BROMINE IN SOLUTIONS OF BROMINE CHLORIDE

Reagents

These were all of analytical grade.

Potassium cyanide: 5% solution, neutralised with sulphuric acid in the presence of methyl red as indicator.

Carbon dioxide: from steel flask.

Chlorine water: freshly prepared, free from bromine.

Potassium iodide: solid.

Hydrochloric acid: 20% distilled (bromide-free), prepared according to Pharm. Hung. V, Vol. I, p. 295.

Sodium Thiosulphate: $0{\cdot}01N$.

Sodium hydroxide: $2N$,

Sulphuric acid: $2N$.

Method

A 10·00 ml portion of the approximately $0{\cdot}1N$ stoichiometric solution of bromine chloride to be tested is transferred to a 100-ml Erlenmeyer flask with a ground glass stopper, and is mixed, in a well-ventilated hood, with 2 ml of 5% potassium cyanide solution previously neutralized in the presence of methyl red indicator. Carbon dioxide is bubbled through the solution at a vigorous rate for half an hour, in order to remove excess bromine cyanide and hydrogen cyanide. The solution is neutralised in the presence of methyl red indicator and chlorine water is added dropwise until the liquid turns light straw-yellow. Half as much 5% potassium cyanide solution is added as the volume of added chlorine water. The liquid is shaken and allowed to stand for 2–3 minutes and 0·2 g of potassium iodide is added to the reaction mixture which is acidified with 5 ml of 20% hydrochloric acid. After allowing the liquid to stand for 20 minutes, the amount of liberated iodine is measured by titration with $0{\cdot}01N$ sodium thiosulphate solution.

1 ml of $0{\cdot}01N$ sodium thiosulphate solution is equal to 0·1998 mg (log 0·30060) of bromine. Half of the total quantity of elementary bromine (Br_2) was removed as bromine cyanide and the titration indicates only the residual amount of bromide ion. Thus, the equivalent weight is one-quarter of the atomic weight.

On investigating in this way a solution of bromine chloride of stoichiometric composition, it was found that 1–3% of bromine forms during homolytic dissociation (Table 1).

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[4] L. Molnár, Dissertation in manuscript.
[5] F. W. Bennett and A. G. Sharpe, *J. Chem. Soc.*, 1950, 1383.
[6] E. Schulek and K. Burger, *Acta Chim. Hung.*, in press.
[7] L. J. Lambourne and P. W. Robertson, *J. Chem. Soc.*, 1947, 1167.

Talanta, 1959, Vol. 2, p. 283. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

A comment on the purity of water prepared by ion-exchange methods

SIR:

Schenkel and Kitchener (*Nature*, 1958, **182,** 131) have recently reported that conductivity water prepared by ion-exchange methods produces anomalous surface effects which they attribute to traces of a weakly basic substance, probably polymer fragments dissolved from the resin. We also have observed evidence of such contamination and agree with these authors that the "conductivity value is a dangerous index" of the purity of water treated with an ion-exchange resin. It is our experience that the contaminant appears to be removed by passage through Millipore filters (Millipore Filter Corp., Watertown, Mass.). This work is described fully in an article entitled "The Nucleation and Precipitation of Silver Chloride from Homogeneous Solution", to appear in this journal.

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LOUIS GORDON

27 *March* 1959

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OBITUARY

THOMAS BROOKS SMITH

The death of Dr. T. B. Smith at his home in Sheffield on Friday, 21st November, 1958, although coming after several years of comparatively poor health, was nevertheless very unexpected. He had retired prematurely in December 1956 from his appointment as Senior Lecturer in Analytical Chemistry in the University of Sheffield and had hoped to make use of his retirement to fulfil many of the tasks that a busy life had inevitably left undone. He had become a member of the Advisory Board of this journal when it was founded.

Thomas Brooks Smith was born in Newcastle-upon-Tyne in the year 1893, was educated at Hull and then studied chemistry at Imperial College, London (then the Royal College of Science), where he came under the influence of J. C. Philip and T. E. Thorpe. In 1914 he took a junior post in the chemistry department of the University of Sheffield which at that time was one of the youngest of the provincial universities. Conditions were difficult and the department was highly under-staffed by modern standards, but the requirements of war service soon took "T.B." (he was always known as "T.B.") off with the allied army as Divisional Gas Officer to Salonica, where his outstanding personal qualities of resourcefulness and ingenuity saw him safely through those grim years.

After the war, in 1919, "T.B." returned to Sheffield as lecture-demonstrator, but soon became involved in the tremendous task of organising and equipping the chemistry department to meet the new demands of the post-war situation. Professor W. P. Wynne soon gave him complete charge of all teaching of inorganic chemistry above the intermediate level, and this position "T.B." retained until his retirement in 1956. The only facilities afforded during the whole period—nearly forty years—comprised a temporary laboratory in a wooden hut; this hut was only removed when the new chemistry buildings came into use in 1955.

It will for ever remain a mystery how "T.B." managed to find either space or time to carry out his research projects; his experiments were always done in some odd corner of this teaching laboratory and suffered constant interruption by reason of the never-ending demands of enthusiastic students. Despite these difficulties many analytical problems were investigated and solutions found, though of these only a small proportion ever reached the stage of publication in research journals.

Experimental work was always done in short bursts of rather feverish activity, alternating with longer periods of quiet rumination during which his active mind would be at work on some new idea which would eventually form the nucleus of another investigation. Even during the active periods, however, a serious enquirer seeking advice was never refused a hearing. Indeed, the enquirer could always expect a lengthy and objective discussion of the problem from every possible point of view, with perhaps a trip to the library to ensure that no stone be left unturned in obtaining every grain of information; but after all this he would be left to think the problem out anew and to draw his own conclusions.

As a teacher "T.B." never gave a simple and straightforward presentation of subject matter with all the difficulties judiciously ironed out—the method so much beloved by bad students. His process instead was to awaken the student to the realisation that things are not always as simple as they seem, that many of the views commonly accepted even by the writers of textbooks will not bear more than superficial exploration without revealing alarming weaknesses, and that ability to think in quantitative terms is of the essence of progress in a subject where tradition sometimes tends to over-ride critical judgment. It is no cause for surprise that his examination questions were always highly unconventional and that his lecture times tended to disregard the clock. His lecture demonstrations did not usually involve elaborate apparatus but were always very much to the point and were expertly carried out.

The final outcome of his many researches into, and thoughts about, analytical methods was the publication of the book *Analytical Processes* for which his name is so well-known. In it the reader may discover for himself the profundity and keenness of its author's mind and the originality with which the problems are treated. Many generations of students have perused its pages and have there discovered the results of concentrated study and active thought about all those processes which are most important to the analyst; from it they will have learned how to tackle new problems, how to discover where the main dangers lie, and how best to seek for a solution. The book is without doubt a landmark in the development of analytical theory, and the change that has taken place in analytical thinking since its first publication in 1929 reveals how much ahead of his day the author was.

But T. B. Smith was much more than a good scientist. He put his unusual degree of manual dexterity to good use in watch-making, in piano-playing, and in repairing anything of a mechanical nature that came his way. No household gadget was allowed to escape his dissecting enthusiasm, and the domestic inconvenience caused by this quality was at times considerable. He was also a conjuror of quality, giving displays that were always elaborately planned to suit the occasion.

Finally, "T.B." would be the first to want to acknowledge the tremendous debt that he owed to his wife Ursula, whom he married in 1927 and who survives him. She it was who accomplished the difficult task of getting the ideas contained in *Analytical Processes* into print, who put his work before all other interests, who nursed him through his many illnesses and who gave to him the ideal counterpart to his own rather wayward temperament. Among the many interests that they shared, the study of ethical and philosophical problems loomed large, and all who knew "T.B." were aware that he was a man not merely of wide knowledge and true understanding but that he possessed the much rarer gift of wisdom. His insight even in problems far removed from his special field was remarkable, and he certainly believed that there are more things in heaven and earth than are dreamed of in the average scientist's philosophy. His death is indeed a great loss both to his friends and to the world of analytical chemistry.

P. WOODWARD

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BOOK REVIEWS

Elementary Practical Organic Chemistry, Part III. Quantitative Organic Analysis. ARTHUR I. VOGEL. Longmans, Green and Co., London, 1958. Pp. xii + 645–840 + xxxii. 21s.

A GOOD maxim for every chemist to remember is that everything depends ultimately on quantitative analysis. Thirty years ago the research, and often the honours student, had to perform a number of quantitative experiments such as carbon and hydrogen, nitrogen, alkoxyl, halogen and acetyl determinations; the accuracy required for success added greatly to the skill of the operator. In these days of micro and semimicro specialists the quantitative aspects of organic analysis tend to be neglected; this volume will give a new stimulus to students and teachers alike. The author is well-known for his previous books on analysis; the present small volume is the last of his recent trilogy, the preceding ones having dealt with small scale preparations and qualitative organic analysis repectively; he has now covered the whole field of organic laboratory work. The chapter, page and section numbers run continuously throughout the trilogy which has also appeared as an omnibus volume.

Semi-micro methods for determining nitrogen, halogens and sulphur, with descriptions of apparatus are given; it seems a pity that the now equally important phosphorus and fluorine determinations are not included. The general account of titration in non-aqueous solvents covers modern ideas on acids and bases and discusses their titrations with indicators. A special feature is made of this type of titration and many examples occur in the text under, for example, amines, phenols, acids, enols. Potentiometric titration is also exemplified with diagrams of suitable apparatus.

Succeeding chapters deal with the estimation of the following:—hydroxyl (alcohols, α-glycols, phenols); amino; amine, including quaternary ammonium, salts; amino-acids; carboxyl and salts; anhydride; ester; carbonyl; sugars; nitro, nitroso, azo; unsaturation; alkoxyl; C-methyl; N-acetyl; active hydrogen; enol; imide; sulphonamide; thiol; sulphide; disulphide; α-epoxy. The use of ion-exchange resins, the Karl Fischer reagent and special determinations complete the list.

Each section begins with a brief outline of the reaction, with equations; often two, or more, types of determination are described under the headings "Reagents" and "Procedure", *e.g.* for glycols both the iodometric and acidimetric methods are given, with five and two examples respectively. The "Calculation" of results is finally detailed. Some methods are not up-to-date, for instance the acetylation of phenols and especially of alcohols.

Many standard methods for determining unsaturation are given. Catalytic hydrogenation is described for platinum oxide and Raney nickel (stabilized) catalysts, but no mention is made of palladium catalysts which are often so useful and selective with double bonds. Both the Wijs and the Hanus methods for determining iodine numbers, and the bromate-bromide and the pyridine sulphate dibromide methods for unsaturation are included.

Active hydrogen is estimated by the older Zerewitinoff reaction (methyl magnesium iodide in anisole, ether, etc.), and by the more recent lithium aluminium hydride method. The section on anion- and cation-exchange resins gives a general outline of the principles involved; a few suitable resins are mentioned and there is a list of salts of organic acids and of a few organic bases which give good results in ion-exchange chromatography. Procedures include salts of organic acids, salts of organic bases, alkaloidal salts, and saponification equivalents of esters.

The Karl Fischer reagent is described in some detail. It is useful in determining the water content of (listed) hygroscopic and water-miscible liquids and of water of crystallization (some examples). It has also been employed in a number of reactions with other substances of which the following are mentioned:—organic acids, anhydrides, carbonyl compounds, primary and secondary amines, cyanides, The preparation of the reagent and apparatus for its use are detailed. Hydroxyl in all classes of monohydric alchols may also be determined by this method.

Special methods include:—formaldehyde (two reactions); acetone; aryl hydrazines; urea (two methods); organic peroxides and hydroperoxides; *iso*thiocyanates and *iso*cyanides; carboxyl by the *iso*thiuronium salt method and subsequent titration with acetous perchloric acid; alcohols.

The following items form an appendix:—atomic weights; bibliography of 15 works on quantitative organic analysis; vapour pressures of water; four- and five-figure logarithms.

Any student who masters all the techniques described here will emerge with confidence to perform any practical problems which the future may hold for him.

A. McGookin

The Chemical Behavior of Zirconium. Warren B. Blumenthal. D. Van Nostrand Company Inc., Princeton, N.J., New York, Toronto, London, 1958. Pp. 398 + vi. $11.00.

In the preface the author tells us that only one book has previously appeared on the chemistry of zirconium, in 1922. His task has included therefore not only a coverage of both the earlier and more recent literature on zirconium but also a recasting of the earlier literature into contemporary language and theoretical understanding.

The nine chapters are headed:— The Element, Zirconium; Interstitial Solutions and Intermetallic Compounds; Zirconium Halogenides; Zirconium Oxides and the Zirconates; Zircon and the Complex Silicates; The Sulfatozirconic Acids, Sulfates, and Sulfonates; Compounds of Other Inorganic Acids; Carboxylates of Zirconium; Organic Compounds Other than the Carboxylates. The inorganic analyst who has to deal with this not so rare metal can read them all with profit: chapter 4 on the oxides and the zirconates and chapters 7, 8 and 9 on the compounds of inorganic acids, the carboxylates, and organic compounds other than the carboxylates, are especially important.

The reverence in which the reviewer has always held Berzelius is deepened by the number of references to his early work with this element. His metal prepared in 1824 was 93·7% Zr but eighty years later it was found that his reaction product could be 98% pure if it was first treated with absolute alcohol instead of water and then washed with dilute acid. He made the carbide as early as 1817 and his figure of 89·46 for the atomic weight compares favourably with the present value of 91·22 when allowance is made for the oxygen content.

In the chapters on the carboxylates and on other organic compounds there is much of interest to the analyst. The almost unique reaction with mandelic acid is discussed (p. 335) and on page 340 we learn that "The zirconium atom is practically never available for reactions which occur by the pairing of oppositely charged ions or by the pairing of odd electrons," and again, "after its reactions, zirconium must always contain at least 8 electrons in its valence orbitals (4d and 5sp) and all reactions of zirconium may be regarded as initiated by the donation of lone pairs of electrons from other atoms to the zirconium atoms."

The price of this book seems high by British standards but it is a most authoritative work and lives up to the claim on the cover that it "brings unity and clarity to a mass of miscellaneous data." It can be recommended without reserve.

R. C. Chirnside

methods); organic peroxides and hydroperoxides; *iso*thiocyanates and *iso*cyanides; carboxyl by the *iso*thiuronium salt method and subsequent titration with acetous perchloric acid; alcohols.

The following items form an appendix:—atomic weights; bibliography of 15 works on quantitative organic analysis; vapour pressures of water; four- and five-figure logarithms.

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R. C. Chirnside

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NOTICES

The following meetings have been arranged:

Monday-Friday 22 *June*-3 *July* 1959: Residential Course on *Radiation Health Hazards:* Wolverhampton and Staffordshire College of Technology, Wulfruna Street, Wolverhampton: Organisers: F. SCOTT, B.Sc., F.R.I.C. and E. WILLIAMS, B.Sc., A.Inst.P.

Although primarily intended for safety officers in Technical Colleges, applications are also invited from others interested in this aspect of the usage of ionising radiations.

Friday 26 *June* 1959: **Polarographic Society: Society for Analytical Chemistry,** Scottish Section: Symposium on *Polarography.* This joint meeting will be held in the Department of Chemistry, David Keir Building, The Queen's University of Belfast. Papers will be presented between 10.0 a.m. and 12.30 p.m., and between 5.0 p.m. and 7.0 p.m. in the Lecture Theatre of the Department of Chemistry. In the afternoon there will be a tour of the Laboratories of the new Building.

The programme of papers is as follows:—

The Polarographic Investigation of Some Copper Complexes in Non-aqueous Solution: Dr. Z. ZAGORSKI, Chemistry Dept., Q.U.B. and University of Poznan, Poland.

Aspects of the Polarographic Behaviour of Rhenium and Technetium: Dr. R. J. MAGEE, Chemistry Dept., Q.U.B.

The Application of Polarography to Tissue Respiration: Dr. I. S. LONGMUIR, Institute of Diseases of the Chest, London.

A Potentiometric Method for Acid-base Titrations in Certain Acetone-water solutions: Mr. G. F. REYNOLDS, Chemical Inspectorate, Woolwich Arsenal.

The Polarographic Determination of Nitroglycerine: Mr. A. F. WILLIAMS, I.C.I. Ltd., Nobel Division.

Polarography in Fused Salts: Mr. R. L. FAIRCLOTH, U.K.A.E.A., Harwell.

A limited amount of accommodation will be available as required in University Hostels; if hotel residence is preferred, intending delegates are requested to make their own arrangements.

Anyone intending to be present at this meeting should notify Mr. J. Brooks (Hon. Secretary, S.A.C., Scottish Section), Analytical Research Section, Research Department, I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire, as soon as possible stating whether University Hostel accommodation is required.

Monday-Friday 6-17 *July:* Residential Course on *Spectrochemical Techniques:* Wolverhampton and Staffordshire College of Technology, Wulfruna Street, Wolverhampton, Staffs. Course Tutor: W. B. FOSTER, B.Sc., A.R.I.C.

This course is intended to cover the fundamental theoretical and practical aspects of emission spectrography, ultra-violet and infra-red spectrophotometry, and flame photometry. Emphasis will be placed on practical work in all branches, and there will be opportunity for course members to select techniques for more detailed study. Additional evening lectures will be given by visiting specialists.

Wednesday-Saturday 9-12 *September* 1959: **Polish Chemical Society:** *Sixth Jubilee Congress.* The Polish Chemical Society is organising the Jubilee Congress in honour of the 40th Anniversary of the Society. The Congress will be held in Warsaw. General meetings and section meetings will be devoted to plenary lectures and short communications. The following sections are planned: inorganic chemistry, organic chemistry, physical chemistry, analytical chemistry, radiochemistry and chemical technology and engineering. A three-day excursion programme to Cracow, Oswiecim and Wieliczka is planned in connection with the Congress. The address of the Organising Committee is Warszawa, Palac Kultury i Nauki, pokòj 2011, Poland.

Thursday-Saturday 1-3 *October* 1959: **Verein Österreichischer Chemiker:** In conjunction with I.U.P.A.C. In the II Chemischen Universitäts-Institut, Vienna, IX, Währingerstrasse 38. The meeting will be concerned chiefly with electrochemistry, and especially with electrocrystallisation. Those wishing to contribute should notify the Sekretariat des Verein Österreichischer Chemiker, Wien, I, Eschenbachgasse 9, Austria, before 30 June. It is hoped to be able to distribute the programme of the meeting in July 1959.

Monday-Wednesday 26-28 *October* 1959: **Oak Ridge National Laboratory:** Third Conference on *Analytical Chemistry in Nuclear Reactor Technology: The Analysis of Reactor Materials Following the Operation of Nuclear Reactors.*

The Oak Ridge National Laboratory has announced that the Third Conference on Analytical Chemistry in Nuclear Reactor Technology will be held at Gatlinburg, Tennessee, on October 26, 27 and 28, 1959.

The general theme of this conference, analysis of reactor materials following the operation of nuclear reactors, complements sequentially those of previous meetings which dealt with, (1) advances in the chemical analysis of important reactor materials, and (2) the role of analytical chemistry in the startup and operation of nuclear reactors.

The subjects which will be emphasized at this conference are: chemical analysis as related to the estimation of corrosion and erosion rates, re-processing of fuels and blanket materials, and the analytical chemistry of fission product mixtures, of plutonium, and of the transplutonic elements.

The contribution of papers pertaining to these or closely related subjects is solicited. Presentations on new developments or improvements in methods of chemical analysis, including advances in instrumentation, are especially invited although review papers and those involving pertinent theoretical discussions may well prove to be of equal interest and should be submitted for consideration.

To facilitate the completion and distribution of the programme well in advance of the conference, speakers are requested to submit abstracts of about 500 words not later than August 1, 1959, and to indicate the time required for their presentation, not to exceed 30 minutes.

The Proceedings of the conference will be published. In order to be included in the Proceedings, manuscripts must be submitted before the opening of the conference. Publication in the Proceedings is not mandatory, but desirable. If a paper is not to be published in the Proceedings, the abstract and a reference to another source of publication, if any, will be made.

All communications relative to the conference, including the submission of manuscripts and abstracts, should be directed to: C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box Y, Oak Ridge, Tennessee, U.S.A.

Inquiries with respect to accommodations or requests for reservations should be addressed to: Mr. TOM WOODS, Manager, Mountain View Hotel, Gatlinburg, Tennessee, U.S.A.

Probably a morning and afternoon session will be held on each of the three days of the conference. If greater interest is evidenced in certain aspects of this subject matter, arrangements will be made to increase the number of sessions but within the scheduled period of three days. Every effort will be made to avoid conflicts of interest in scheduling concurrent sessions.

Since it is intended that the scope of the programme will necessarily encompass only a limited portion of the field of analytical chemistry as it pertains to the analysis of materials after they have been involved in an operating reactor, the general topics for each of the six sessions will be essentially as follows:

Monday 26 *October*

Morning—*The Analysis of Spent Reactor Fuels*
Afternoon—*Analytical Chemistry of Exposed Blanket Materials*

Tuesday 27 *October*

Morning—*Analytical Chemistry in the Reprocessing of Fuels and Blanket Materials*
Afternoon—*The Analysis of Corrosion and Erosion Products*

Wednesday 28 *October*

Morning—*The Analysis of Fission Product Mixtures*
Afternoon—*Analytical Chemistry of Plutonium and Transplutonic Elements*

In addition to the formal technical programme, an informal dinner and dance will be held on Tuesday evening. Arrangements are now being made to secure a prominent speaker in the field of analytical chemistry or some closely related field to address the group after the dinner.

The conference is being conducted on an unclassified basis and all interested persons, regardless of affiliation, are invited to attend or participate in all or any portion of the meeting.

There will be no registration fee, but for those who partake of the dinner a nominal charge will be made.

The *B.S.I. News* announces, among others, the following new standards:

BS 2511 (PD 3201): *Determination of water by the Karl Fischer method:* Addendum 1, 1959: *Determination of water in ketones.* This indicates the modifications required to the methods given in Parts 1 and 2 of the standard to enable water to be determined in ketones by the Karl Fischer method using an electrometric end-point. (Price 2s.)

BS 1121: *Methods for the analysis of iron and steel:* Part 39, 1959: *Nitrogen in steel.* This specifies a method applicable to all types of steel containing up to 0.25 per cent of nitrogen. Using this method, complete nitrogen recovery cannot be obtained from steels containing silicon nitride. (Price 4s.)

BS 1902 (PD 3325): *Methods of testing refractory materials:* Addendum 2, 1959: *Additional methods.* This specifies an alternative method for the determination of silica and methods for the determination of size, bulk density and warpage. Full details of the individual methods are given. (Price 3s.)

Revised British Standards have been issued as follows:

BS 350, 1959: *Conversion factors and tables,* Part 1, *Basis of tables, Conversion factors.* The scope of Part 1 of B.S.350 has been considerably augmented by its revision, and now covers a wide range of subjects of measurement falling under the general headings Metrology, Mechanics and Heat. Part 1 gives extended basic information on units, together with the standard abbreviation for each unit or combination of units considered. The standard does not deal with purely electrical units. A feature of the standard is the inclusion of comprehensive tables of conversion factors, showing the relationship between any pair of units used in the measurement of a given physical quantity. Summary tables of units and conversion factors are included, together with an appendix on thicknesses of sheets and diameters of wires. A list of the detailed conversion factors which will be included in Part 2 is also given. (Price 15s.)

B.S. 753, 1959: *Density-composition tables for aqueous solutions of sulphuric acid.* The tables, based on the International Critical Tables, give density in grams per millilitre of the aqueous solution, mass in grams of H_2SO_4 in 100 grams of aqueous solution and mass in grams of H_2SO_4 in 1 litre of aqueous solution. Notes on the use of B.S. density or specific gravity hydrometers are added, including the corrections to be applied in various circumstances, with worked examples. (Price 15s.)

B.S. 903: *Methods of testing vulcanised rubber:* Part B 17, 1959, *Determination of total copper.* This gives details of reagents and procedure. (Price 3s.)

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

Talanta, 1959, Vol. 2, p. 291. Pergamon Press Ltd. Printed in Northern Ireland

BOOKS RECEIVED

Laboratory Distillation Practice. E. A. COULSON and E. F. G. HERINGTON. George Newnes Limited, London, 1958. Pp. x + 166. 25s.

Laboratory Glassblowing. L. M. PARR and G. A. HENDLEY. George Newnes Limited, London. 1956. Pp. iv + 160. 21s.

Annotated Bibliography of Alpha-Benzildioxime. CHARLES V. BANKS, MICHAEL J. MAXIMOVICH, NELSON J. FOWLKES and PETER A. BEAK. United States Atomic Energy Commission, Research and Development Report ISC 1038. 1958. $1.75.

Tables of Constants and Numerical Data. Pergamon Press, Ltd., London and New York. **Vol. 9, Pouvoir Rotatoire Naturel, II. Triterpènes.** J.-P. MATHIEU and G. OURISSON. Pp. 302. 1958. £7. **Vol. 10, Pouvoir Rotatoire Naturel, III, Amino-Acides.** J.-P. MATHIEU, P. DESNUELLE and J. ROCHE. Pp. 61, 1959. 40s.

Talanta 1959, Vol. 2, p. 292. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

New Contributions to the Halogenating Effect of Iodine Bromide. E. Schulek and K. Burger. (20 *March* 1959).

Contributions to the Chemistry of Selenium and Selenium Compounds-II. New Contributions to the Iodometric Measurement of Selenocyanide. E. Schulek and L. Barcza. (20 *March* 1959).

Contributions to the Chemistry of Selenium and Selenium Compounds-III. Microdetermination of Selenite through Bromocyanogen. E. Schulek and L. Barcza. (20 *March* 1959).

Contributions to the Chemistry of Selenium and Selenium Compounds-IV. Detection and Determination of Minute Amounts of Selenite in the Presence of Selenate. E. Schulek and L. Barcza. (20 *March* 1959).

Solvents for Ultraviolet Spectrophotometry. D. D. Tunnicliff. (2 *April* 1959).

An EDTA-Polarographic Method for the Determination of Tellurium in the Presence of Lead. Zbigniew Zagorski and Maria Cyrankowska. (6 *April* 1959).

The Determination of Ultramicro Quantities of Silver in Platinum Sponge by Neutron Activation Analysis. D. F. C. Morris and R. A. Killick. (9 *April* 1959).

Vereinfachte Schnellmethode zur Sulfatbestimmung durch Ionenaustausch. J. A. Mikes and J. Szántá. (20 *April* 1959).

Bestimmung der Abriebfestigkeit von Ionenaustauschern. J. A. Mikes and L. Kovács. (20 *April* 1959).

Organic Analysis-XV. Some Observations on the Infrared Spectra of the Tetralin Series. Tsutomu Momose, Yo Ueda and Hiroshige Yano. (22 *April* 1959).

The Redox Properties of Some Alkoxyl-Substituted Benzidines. D. I. Rees and W. I. Stephen. (5 *May* 1959).

The Wet Oxidation of Bone: Digestion with 100 per cent Sulphuric Acid Followed by the Addition of Dioxonium Perchlorate. G. Frederick Smith and Harvey Diehl. (12 *May* 1959).

Komplexometrische Bestimmung von Bor neben Barium. Otto Borchert. (14 *May* 1959).

Utilisation of Ternary Complexes in Chemical Analysis, I. Selective Extraction and Colorimetric Determination of Traces of Iron as "Ferroin Iodide." Frantisek Vydra and Rudolf Přibil. (14 *May* 1959).

Spectrophotometric Determination of Thorium with Neo-thorone. Takeo Takahashi and Shingo Miyake. (16 *May* 1959).

Studies on Uronic Acid Materials, II. The Variation in Composition of Gum Nodules from *Combretum Leonense*. D. M. W. Anderson, E. L. Hirst and N. J. King. (16 *May* 1959).

Analytical Applications of Xylenol Orange, III. Spectrophotometric Study of the Hafnium-Xylenol Orange Complex. K. L. Cheng. (18 *May* 1959).

Titration of Oxalic Acid with Cerium^{IV} at Room Temperature Using Ferroin as Internal Indicator. V. Panduranga Rao and G. Gorala Rao. (20 *May* 1959).

2-Mercaptoacetic (Thioglycollid) Acid as a Reagent for Zirconium. Suseela B. Sant and Bharat R. Sant. (20 *May* 1959).

A Study of the Conditions for the Determination of Boron with Dianthrimide. Lars Danielsson. (23 *May* 1959).

The Determination of Boron in Iron and Low-Alloy Steels with Dianthrimide: A Colorimetric Method that does not require Preliminary Separations. Lars Danielsson. (23 *May* 1959).

The Application of Zone Electrophoresis and Polarography in the Analysis of Complex Mixtures. W. Hoyle and T. S. West. (25 *May* 1959).

The Polarographic Determination of Nitroglycerine. A. F. Williams and D. Kenyon. (26 *May* 1959).

The Semi-micro Determination of Silicon and Phosphorus in Organic Compounds. T. R. F. W. Fennell and J. R. Webb. (30 *May* 1959).

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BENZIDINE AND ITS DERIVATIVES IN ANALYTICAL CHEMISTRY

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Summary—A survey has been made of the analytical applications of benzidine and diphenylamine and their derivatives, as precipitants, in the detection and colorimetric determination of oxidants and as indicators in titrimetric analysis. The period covered is from the beginning of 1946 to the end of 1958.

BENZIDINE (4:4′-diamino-1:1′-diphenyl) is the parent of an important group of organic reagents used in chemical analysis. It includes nuclear-substituted and N-substituted benzidines and the diphenylamines since diphenylamine has been shown[1,2] to oxidise to N:N′-diphenylbenzidine (probably through N:N′-tetraphenylhydrazine) and then to diphenylbenzidine violet.

The analytical applications of this class of compound have been surveyed by Welcher[3] up to 1946. This review discusses new applications of the reagents covered by Welcher; it also deals with new reagents, structurally related to benzidine, which have been developed and reported in the literature between 1946 and the end of 1958.

Benzidine owes its versatility as an organic reagent to the amino groups and their arrangement in the molecule. These groups confer on it the properties of complex formation with metal cations and of salt formation from acid solution; in addition, the arrangement of the groups in the diphenyl nucleus is responsible for the formation of highly coloured products on oxidation and at least partially responsible for the insolubility of certain salts and complexes.

Benzidine is not now used in the gravimetric analysis of metals because of the availability of more selective precipitants, giving better defined products, and the increased use of titrimetric and instrumental methods of analysis. Considerable interest has been shown in the salt-forming properties of this class of compound, particularly for sulphate precipitation and for the precipitation and fractionation of mixtures of polyphosphates and polythionates. However, reactions involving the oxidation of benzidine type compounds have received most attention and have been applied mainly in spot test reactions, and in colorimetric, absorptiometric, and titrimetric methods of analyses.

PROCEDURES DEPENDING ON PRECIPITATION

Sulphate

A few indirect methods for analysis of sulphate, based on precipitation with benzidine, have been proposed. Andersen[4] has determined sulphate by precipitating as the benzidine salt, dissolving the precipitate in a measured volume of dilute hydrochloric acid and measuring the absorbance at 250 mμ with a spectrophotometer.

In this way sulphate is determined in samples containing as little as 1 to 25 μg sulphur. The benzidine precipitate with sulphate has been digested with lead nitrate, the resulting lead sulphate being dissolved in an acetate buffer and the lead determined by amperometric titration. The working time and accuracy of this method is claimed to be comparable with that of the gravimetric procedure.[5] Sulphate can also be determined by direct conductometric titration with standard benzidine dihydrochloride using a 30% ethanol-aqueous solution and working in the pH range 4 to 7. Errors of about 1% may be expected in the 1-mg to 40-mg sulphur range, but the method has the advantage of being rapid.[6] Phosphate if present must be removed. Benzidine sulphate is stable between 70 and 156° and is best dried between 72 and 130° in the gravimetric determination.[7] *o*-Tolidine (3:3′-dimethylbenzidine) is not recommended for sulphate determination.

Two serious disadvantages of benzidine as a reagent for sulphate are the appreciable solubility of the sulphate and the non-selective nature of the precipitant. The solubility of the sulphate is 0·098 g per litre at 25° in neutral solution and rises to almost 10 times this value in 0·5*N* hydrochloric acid. Phosphate, molybdate, tungstate, iodate, ferricyanides and ferrocyanides and many cations are also precipitated by benzidine. However, it has the advantage over barium of not being affected by moderate amounts of chloride or nitrate.

Within the last ten years, efforts have been made to find other amines possessing advantages over benzidine as sulphate precipitants. A study of the solubility of the sulphate salts of substituted benzidines and related compounds by Belcher and Nutten[8] led to an investigation[9] of the effect of replacement of one amino group in benzidine by halogen. The sulphate solubilities of the four possible 4-amino-4′-halogenodiphenyls indicated that all of these amines would be superior to benzidine in removing sulphate from solution. Of these potential reagents, 4-amino-4′-chloro-1:1′-diphenyl is most suitable for sulphate determination as it has the highest hydrochloride solubility in water (*ca.* 0·35%) and the greatest sensitivity. Sulphate has been precipitated with this reagent at pH 1 to pH 2 with a twofold excess of reagent and a standing time of 20 to 30 minutes.[9,10] The sulphate in the precipitate is determined by suspending in water and titrating with standard caustic alkali. Oxidising agents, except hydrogen peroxide interfere, but halide, nitrate, acetate, citrate and tartrate do not interfere. Phosphate, tellurite, selenate and oxalate interfere through formation of insoluble salts. Oxalate and phosphate are removed by calcium. Zinc, copper and magnesium ions tend to form soluble complexes with the reagent but can be tolerated in tenfold amounts. Ferric, chromic, calcium and alkali metal ions do not interfere but aluminium tends to form an insoluble complex containing sulphate unless tartaric acid is present. The sensitivity of the reagents toward sulphate is superior to that of the barium ion but later work has shown that the solubility of the precipitate is higher (*ca.* 10 times) than had been reported initially. It is well known that the solubility of a substance is not a constant and it seems likely that the method of precipitating and drying the sulphate salt used by Belcher, Nutten and Stephen would lead to a lower observed solubility than that found for the sulphate precipitated from an aqueous solution under the conditions employed in an actual determination. This work[10] also indicates the necessity for care in the use of the reagent, in particular in adjusting the acid concentration of the test and reagent solutions before precipitation, and in the addition of the optimum excess of reagent (*cf.* Bengtsson[11]).* The addition of a little paper-pulp to the test solution before precipitation is advantageous and care is necessary in preparing the pulp-pad and in its actual use in filtering off the precipitate. Another disadvantage of the reagent is the low solubility of the amine hydrochloride in water, necessitating the use of large volumes of reagent solution. The possible use of other salts of this amine as reagents has been examined but none show any advantage over the hydrochloride.[10]

The reagent, which is undoubtedly the best of its class, is suitable for the micro determination of sulphur in organic compounds containing nitrogen,[12] in coal[13] and in rubber.[14] In each method the sulphate is determined titrimetrically. Jones and Letham[15] have determined 20 μg to 50 μg quantities of sulphate resulting from nucleic acid degradation, by precipitating the sulphate with a measured excess of this reagent and determining the excess in the solution spectrophotometrically. Absorbance measurements are made at 254 mμ. An essentially similar method has been applied to the determination of milligram amounts of sulphur in coal with good results.[16]

From a study of the sulphate solubilities of a range of substituted benzidines and other diamines, Belcher, Kapel and Nutten[17] concluded that co-planarity of the aromatic nucleii in diphenyls and linking of the amino and phenyl groups to each other in the *p*-positions are essential structural characteristics for low sulphate solubility. Electron microscopic studies of the sulphate salt of benzidine led Fischer and Sprague[18] to suggest that incompleteness of sulphate precipitation with benzidine is probably due to imperfect crystal formation and growth caused by a very tight surface adsorption of foreign ions on the growing crystallites.

Molybdate and tungstate

Benzidine hydrochloride will precipitate tungstate completely from neutral solution. The precipitate is insoluble in a solution of the reagent but will pass through a filter if washed with water. Precipitation from hot solution gives a coarser precipitate which is somewhat soluble in hot water and should not be filtered until the solution is cold. Von Knorre[19] showed that precipitation from the cold in the presence of a little sulphuric acid, resulted in good recovery of tungsten. The mixed benzidine tungstate and sulphate is ignited to tungsten trioxide at 800°. Phosphate, except in very small amounts, will interfere, as will molybdate unless the solution is about 0·5*N* to hydrochloric acid. At this acid concentration the tungstate becomes appreciably soluble so that benzidine and also diphenyline (2:4′-diamino-1:1′-diphenyl) is unsatisfactory for tungstate determination in the presence of molybdate.

Belcher and Nutten[20] have examined benzidine, diphenyline and several substituted benzidines and other aromatic amines as precipitants for tungstate in the presence of molybdate. Of the other amines investigated only 4:4′-diaminostilbene and 1-amino-4-*p*-aminophenylnapthalene give virtually quantitative precipitation of tungstate from 1*N* hydrochloric acid. Both molybdate and tungstate are quantitatively precipitated from neutral solution by these two reagents but tungstate is precipitated completely enough for most practical purposes from 0·7*N* hydrochloric acid while molybdate remains in solution. Oxidising agents interfere but ferric iron

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* Since the period which this review is intended to cover ended, a short communication (R. Belcher and W. I. Stephen, *Analyt. Chim. Acta*, 1959, **20**, 197) has appeared refuting Bengtsson's main criticisms.

has no effect on diaminostilbene. However, the diaminophenylnaphthalene reagent is preferable as it is more readily obtained. Iron^{III}, chromium^{III}, copper^{II}, cadmium, aluminium, nickel, zinc, calcium, magnesium, sodium and potassium ions do not interfere.

The tungstate content of the precipitate formed with these reagents is variable. For benzidine, the tungstate content increases with decreasing pH and this has been attributed to *iso*-polytungstate formation.[21]

The tungstate of *o*-dianisidine (3:3′-dimethoxybenzidine), precipitated from diluted acetic acid solution contains 50·2% tungsten and 4·01% nitrogen.[22] The tungsten content of the precipitate is more reliably determined by ignition to tungsten trioxide before weighing. Molybate is completely removed from solutions neutral to methyl orange with *o*-dianisidine. Analyses of the precipitate dried at 80° suggests that it contains 1·792% molybdenum trioxide.[23] Since the solubilities of the sulphate and tungstate of all the 3:3′-disubstituted benzidines investigated are higher than those of the corresponding benzidine compounds, *o*-dianisidine would appear to be less attractive as a precipitant for tungstate or molybdate than benzidine, which itself is unsuitable for the separation of these anions. In view of the indeterminate nature of such tungstates or molybdates it is hardly advisable to weigh the precipitates and apply a factor except perhaps in a "rough" analysis.

Nardelli[24] has investigated the use of benzidine to precipitate the silicododecatungstate ion from hydrochloric or nitric acid solution. Pyrolysis of the white precipitate at 850° gives a composition ratio for the residue of silica to tungsten trioxide of 1 : 12·08.

Phosphates and polyphosphates

Orthophosphate is quantitatively precipitated from neutral or acetic acid solution by benzidine. Phosphate in the precipitate is best determined by titration with standard caustic alkali as in the sulphate determination. If the precipitate is to be weighed it can be washed free from excess benzidine with aqueous acetic acid or ethanol. Oxidants will interfere in the precipitation as will other anions forming insoluble salts under the conditions used for phosphate precipitation. Interference from sulphate can be overcome by dissolving out the benzidine phosphate from the mixed sulphate and phosphate precipitate with 0·1N hydrochloric acid. The phosphate salt with benzidine is reprecipitated by making the filtrate alkaline with aqueous ammonia. However, sulphate is more conveniently removed with barium chloride. Ferric iron must be reduced to the ferrous state and in the presence of aluminium, phosphate must be precipitated from acetic acid solution. Dimethyl hydrogen phosphate reacts quantitatively with benzidine dihydrochloride in solutions neutral to phenolphthalein. Trimethylphosphate is also precipitated but the precipitate is of indefinite composition and contains free benzidine.[25]

Hecht[26] has investigated the precipitation of trimetaphosphates and tetrametaphosphates with benzidine. With neither is precipitation quantitative nor can a separation be effected under the conditions he employed; but over 90% of the trimetaphosphate is precipitated at pH 5 while tetrametaphosphate is precipitated in somewhat better yield over a less restricted pH range (*ca.* 3–5). Graham's salt is precipitated by benzidine dihydrochloride from solutions of pH < 1 and can be separated from mono-, di-, tri- and tetrametaphosphates in this way. The use of various amines including benzidine, *o*-tolidine, *o*-dianisidine and 3:3′-diaminobenzidine as precipitants for straight chain polyphosphates and polymetaphosphates has been examined by Ebel *et al.*[27,28] By using acetic or hydrochloric acid solutions of the reagents and controlling the pH of precipitation, various separations and fractionations are possible. With the most suitable reagents over 90%, but never quantitative precipitation, is obtained from aqueous solutions. Trimetaphosphates and tetrametaphosphates can be separated. Quantitative but non-selective precipitation with benzidine is possible by the addition of alcohol to the reaction mixture.

Polythionates

Benzidine and *o*-tolidine have received attention as precipitants in the fractionation of complex mixtures of polythionic acids. Singer *et al.*[29] have discussed the formation and fractionation of such mixtures. They consider that mixtures of thiosulphate and arsenic^{III} in concentrated hydrochloric acid solution give polythionic acids containing from five up to at least ten sulphur atoms. The mixture is partially separated by fractional precipitation with benzidine (Bnz) or *o*-tolidine. In the highest fraction, Bnz $H_2S_nO_6$, n approaches 12 but in the main portion n has values from 6 to 9. The lowest sulphur-containing fraction ($n \leq 6$) and the highest fraction ($n > 10$) do not yield highly crystalline salts with benzidine as does the middle fraction. By fractional precipitation with benzidine they found that the method advanced by Goehring and Feldmann[30] for the preparation of hexathionic acid from thiosulphate and sulphur monochloride in the presence of concentrated hydrochloric acid, assumed to proceed as follows,

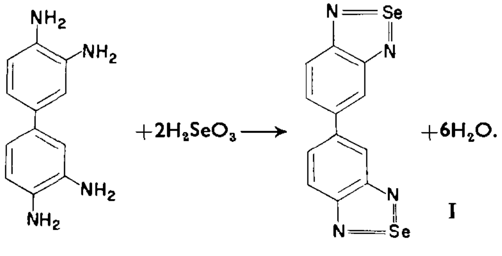
$$S_2Cl_2 + 2H_2O \rightarrow S_2O_2H_2 + 2HCl$$

$$S_2O_2H_2 + 2H_2S_2O_3 \rightarrow H_2S_6O_6 + 2H_2O,$$

actually gives a mixture of polythionates containing from 5 to 15 sulphur atoms. The overall composition of the mixture corresponds to that of hexathionic acid but this acid cannot be freed from other thionic acids by fractional precipitation with benzidine. Yanitskii and Patsauskas[31] found that precipitation of polythionates by benzidine from a reaction mixture similar to that above but using sulphur dichloride in place of the monochloride gave a fraction containing the salts of hepta-, octa-, and nonathionic acids. The preparation of a pure crystalline benzidine salt of octathionic acid has also been claimed.[32]

Miscellaneous salts

Gillis[33] has shown that the reaction between 3:3′-diaminobenzidine and selenite can be made the basis of a sensitive test for selenium. The final precipitate formed, however, is not a simple selenite but a dipiazselenole (I) formed by the following condensation reaction.



I

Tellurium does not interfere but sulphurous acid and 1:2-diketones will interfere through formation of condensation products. Cheng[34] has determined selenium in the 50 μg region by extracting I into toluene and measuring the absorbance of the extract at 420 mμ. Oxidising agents, vanadate, iron^{III}, and copper^{II} ions interfere. The last two mentioned are masked by tartaric or oxalic acid. The method has been applied to the determination of selenium in sulphuric acid.[35]

Shiraeff[36] has used benzidine in the analysis of an ionic detergent, "Igepon T" (the sodium salt of N-methyl oleyl tauride). The salt of this sulphonic acid with benzidine may be weighed or dissolved in alcohol and titrated with standard alkali to phenolphthalein. Suggestions have been made for the extension of the method to other detergents containing sulphonic acid groups and giving insoluble salts with benzidine.[37] Anionic surface active agents are sometimes marketed as salts of nitrogen bases and precipitation of the insoluble benzidine salts of the anionic material leads to a convenient way of distinguishing between nitrogen in the anion and in the associated cation.[38] The benzidine salt is converted to the soluble sodium salt of the anion, leaving free benzidine suspended in the solution. Filtration and evaporation of the filtrate gives the sodium salt of the anionic part of the sample, on which a Kjeldahl nitrogen determination is made. Results suggest that nitrogen contents below 0·5% should be ignored by this method. Such nitrogen possibly arises from small amounts of cation carried down by the benzidine salt in the initial precipitation and from nitrogen in the benzidine dissolved in the final filtrate to be evaporated.

According to Duval,[39] the ferrocyanide and ferricyanide salts with benzidine should be ignited at temperatures exceeding 944° and 975°, respectively, if ferric oxide is to be used as the weighing form. $H_4Fe(CN)_6 \cdot 3Bnz$ would require drying below 52°. Iodate cannot be determined gravimetrically by precipitating with benzidine because of the thermal instability of the salt. Tellurate is removed from solution by benzidine and ignition of the precipitate gives the trioxide.[40]

PROCEDURES DEPENDING ON COLOUR REACTIONS

Many applications of the coloured products resulting from the oxidation of benzidine and related compounds have been recorded in recent years and progress has been made in the inprovememt of the colour stability on oxidation, and in the reversibility and sensitivity of some of the reactions. Improved tests in qualitative analysis and improved procedures in colorimetric and titrimetric analysis have resulted in some instances.

Qualitative tests

It is well known that haematin catalyses the oxidation of benzidine by hydrogen peroxide. Malowan[41] has discussed the effect of salts (Table I) on the reaction as used in clinical and forensic tests for blood. Excess hydrogen peroxide or the presence of ascorbic acid destroys the colour.

Tests carried out with diphenylamine, diphenylbenzidine and nitrodiphenylamine for the detection of the nitrate ion and nitramine explosives in sulphuric acid solution indicate that careful control of the acid concentration is essential.[42] These reagents do not distinguish between nitrate and nitramines, but a difference in rate of colour development is observed when diphenylamine is used to test for *cyclo*-trimethylenetrinitramine and *cyclo*-tetramethylenetetranitramine.

Robinson and West[44] have described a very sensitive test for orthophosphate. It is precipitated as the insoluble *o*-dianisidine phosphomolybdate which is then reduced to a "molybdenum blue" with hydrazine hydrate. In this way, 0·05 μg, at a concentration limit of 1 in 1,000,000, is detected. Apart from sulphide, which interferes through formation of a blue colour after the phosphomolybdate precipitation, the test is almost free from interference from other ions.

TABLE I. THE EFFECT OF SALTS ON THE HAEMATIN CATALYSED HYDROGEN PEROXIDE OXIDATION OF BENZIDINE.

None	Retarding	Intensifying
KCl, NaCl, NH_4Cl, $AlCl_3$, $HgCl_2$, K_2SO_4, $CaSO_4$, $Al_2(SO_4)_3$, $HgSO_4$ $Pb(OAc)_2$	$MgCl_2$, $CaCl_2$ $ZnCl_2$, $(NH_4)_2SO_4$, $MgSO_4$, $ZnSO_4$.	$AcONH_4$ $(NH_4)_2HPO_4$.

N-Phenylanthranilic acid has been recommended in place of benzidine in the detection of chlorate.[44] In the macro test, 1 ml of test solution is mixed with 0·1 ml of a 0·1% reagent solution in alkali and 0·1 to 2 ml of concentrated sulphuric or hydrochloric acid is added. A violent raspberry colour at the interface in sulphuric or a pink colour in hydrochloric acid indicates chlorate in the absence of other oxidants. In the micro test, the test drop, taken to dryness, is treated with one drop of reagent solution and one drop of acid. In sulphuric acid, amounts of chlorate down to 1 μg at a dilution limit of 1 part in 1,000,000 and 0·016 μg at 1 in 1,250,000 are detected by the macro and micro methods respectively. In hydrochloric acid, 1·5 μg at a dilution limit of 1 in 670,000 by the macro method, and 0·08 μg at 1 in 250,000 by the micro method, are detected. There are few interferences from anions and cations apart from oxidants. Bismuth^{V} and nitrate interfere in sulphuric acid but not in hydrochloric acid. Perchlorate does not interfere.

A micro test for thallium in alkaline solution with benzidine and ferricyanide has been proposed by Feigl and Goldstein.[45] The test solution is treated with one drop of a 1% ferricyanide solution and, after standing 30 minutes, with one drop of an acetic acid solution of benzidine. A blue colour indicates thallium. The least amount detected is 1·2 μg at a dilution limit of 1 in 100,000. Lead, if present must first be precipitated with ammonia. Lead in oils and varnishes may be detected with benzidine, after precipitation with alkali and oxidation with bromine water.

Naphthidine and 3:3′-dimethylnaphthidine, in the presence of ferricyanide, have been examined as reagents for the detection of zinc.[46] The latter amine is ten times as sensitive as the former and is less affected by changes in acid concentration. The reagent consists of one part of a 5% solution of potassium ferricyanide mixed with two parts of a saturated solution of naphthidine or dimethylnaphthidine dihydrochlorides. The identification limits on a spot tile for one drop each of test and reagent solutions are 1 μg and 0·1 μg at dilution limits of 1 in 50,000 and 1 in 500,000 respectively. Metal ions giving sufficiently insoluble ferrocyanides will interfere with this test.

Dimethylnaphthidine gives sensitive colour reactions with other oxidants such as dichromate, permanganate, and vanadate. A 1% solution of this amine in acetic acid provides a sensitive test for vanadate.[47] On a spot tile the limit of identification is 0·1 μg at a concentration limit of 1 in 500,000. Other oxidising agents must be absent. Of other benzidine-type reagents examined only 2:7-diaminofluorene is as sensitive towards vanadate, but the colour produced by this reagent, unlike that with dimethylnaphthidine, fades rapidly after development.

The 3′-sulphonic and 3:3′-disulphonic acids of benzidine have been examined in their reactions with oxidants.[48] The disulphonic acid only reacts with more powerful oxidants like cerium^{IV} and dichromate and is less sensitive than the monosulphonic acid. A specific test of moderate sensitivity for copper^{II} in the presence of thiocyanate has been described using the monosulphonic acid.[49]

Cullinane and Chard[50] have investigated the reactions of 2:7-diaminodiphenylene oxide as a spot test reagent and conclude that it may replace benzidine in several spot tests. The sensitivity is generally higher than for the corresponding benzidine reaction and as it is subject to the same interferences, these are overcome as in the benzidine tests. This conclusion has been confirmed by Belcher and Nutten[51] who compared the sensitivities of benzidine and various substituted benzidines including diaminodiphenylene oxide in neutral and in 0·05*N* hydrochloric acid solutions. They found that for most of the oxidants tested, the last mentioned reagent is about ten times as sensitive as benzidine or the other substituted derivatives examined.

Some new 3:3′-disubstituted naphthidines have been prepared[52] and properties of analytical interest, examined.[53] Replacement of methyl groups in 3:3′-dimethylnaphthidine by ethyl, *n*-propyl or *iso*propyl groups does not alter the sensitivity or colour reaction of the amine with oxidants. On replacement by sulphonic acid groups none of the common oxidants used except iron^{III} give sensitive colour reactions in solutions lower than 2*M* in sulphuric or hydrochloric acid, but a red–violet colour the stability of which increases with increase in acid concentration is obtained in stronger acid solutions. Phenyl groups result in a slight decrease in sensitivity and a colour change to violet instead of purple-red. Substitution by nitro groups gives a yellow product unaffected by oxidants, while by contrast the diaminonaphthidine gives only transient colours with oxidants and is unstable in air. Dimethoxynaphthidine gives a greenish-blue colour of stability intermediate between naphthidine and 3:3′-dialkylnaphthidines but more comparable to the latter in sensitivity towards oxidants.

Feigl and Jungreis[54] have devised a test of micro sensitivity for the detection of mono- and di-N-alkylanilines. The Duff formylation reaction is used to convert the substituted aniline to the corresponding *p*-benzaldehyde. If certain phenols are present they will also be formylated and so must be removed before the test is applied.

Colorimetric methods

The high sensitivities of benzidine and some nuclear-substituted and N-substituted derivatives have resulted in their application in colorimetric and absorptiometric methods of analysis. One of the major drawbacks to most of these reagents is colour instability. This has stimulated interest in the search for derivatives giving more stable colours on oxidation and for improved procedures for the reagents more commonly employed. Substitution *o*- to the amino groups or substitution of the hydrogens on the amino groups results in more stable colours on oxidation but this can be associated with a decrease in rate of colour development and sensitivity suggesting that a balance must be sought between increased colour stability through substitution and decreased rate of reaction, in the most favourable reagents. The effect of N-methyl substitution in benzidine and *o*-tolidine on the sensitivity of the resulting reagents to oxidants has been attributed to steric factors.[55] Compared with the unsubstituted compounds, methyl, ortho to an N-methyl group reduces the sensitivity whereas in the same position to an unsubstituted amino-group, it raises the sensitivity. Suitable N- or *o*- substituents may shield the sensitive oxidised groups increasing colour stability in favourable cases, but when present together may result in "over-crowding" around the nitrogen with adverse effects on the reaction with oxidants.

Benzidine and *o*-tolidine have achieved widespread use in the colorimetric determination of chlorine in water. *o*-Tolidine gives a more stable colour than benzidine but it is customary to employ artificial colour standards because of the colour instability of both reagents, and strict working conditions are necessary. A mixture, in tablet form, containing *o*-tolidine has been patented for this determination.[56]

Kul'berg and Borzova[57] have investigated the use of N:N′-tetramethylbenzidine as an alternative reagent in the determination of chlorine in water. This reagent gives a clear yellow to orange colour on oxidation and the improved colour stability permits more accurate determination of chlorine. The water sample (100 ml) is treated with a 1% solution of the reagent (0·1 ml) in 5% hydrochloric acid and set aside for 10 minutes. The absorbance is read at 470 mμ. Belcher, Nutten and Stephen[58] have made a comparison between the sensitivities of the reactions of several nuclear and N:N′-substituted benzidines including N:N′-tetramethylbenzidine, naphthidine and 3:3′-dimethylnaphthidine, with chlorine in water. Dimethylnaphthidine is more sensitive than any of the other reagents tested and can be used in the absorptiometric determination of chlorine in water. Beer's law is obeyed over a satisfactory concentration range, the colour develops quickly (5 minutes) and is stable for at least 15 to 20 minutes. Acetate ions and mineral acids interfere.

N:N′-diphenylbenzidine finds new applications in the determination of vanadium. Eeckhout and Weynants[59] have made the yellow colour produced by orthovanadate with this reagent the basis of a spectrophotometric method for vanadium. Beer's law is obeyed in the concentration range 1 to 10 μg per ml. The colour intensity depends on pH, amount of reagent, time of colour development, temperature and the presence of other ions, suggesting that considerable experience with such a method would be necessary for satisfactory results. Wrightson[60] has shown that vanadium in petroleum oils, oxidised to vanadate with bromine water, is determined with this reagent in samples containing 0·01 to 0·08 mg V_2O_5. The colour is developed in an aqueous solution containing 50% phosphoric acid (s.g. 1·71) and the absorbance is measured 15 minutes later at 575 mμ. A method based on the colour produced by diphenylamine-4-sulphonic acid on oxidation by vanadate is used for the analysis of vanadium in steel. An attempt is made to correct for excess reagent by measuring the absorbance of the oxidised reagent at 562 mμ and again after reduction of the coloured form with ferrous iron; the difference in the absorbances is proportional to the vanadium content.[61] Milner and Nall[62] have used 3:3′-dimethylnaphthidine for the micro determination of vanadium in ferrous alloys. It is superior to diphenylamine in this determination. Scholes[63] found in his investigation of the possible use of dimethylnaphthidine for the macro colorimetric determination of vanadium in steel, that Beer's Law is obeyed in the concentration range 12·5 to 250 μg vanadium per 50 ml, and that maximum colour intensity is reached in 5 to 10 minutes, remaining constant for about 20 minutes. A mixture consisting of 1 part each of sulphuric and phosphoric acids and 8 parts of water is the most suitable medium for colour development and stability. In the presence of small amounts of chromium, special precautions are necessary in using these reagents.

Iridium is determined photometrically by making use of the deep purple colour resulting from the reaction of *o*-dianisidine with the chloroiridate anion.[64] Other platinum metals and oxidants must be removed before the colour is developed in a strongly acid solution containing acetic acid and sodium acetate.

A detailed study of the use of *o*-tolidine in the absorptiometric determination of gold^{III}, and hence the thickness of electrodeposited gold, has been made.[65] Commercial *o*-tolidine is recrystallised three times from 2*N* sulphuric acid and the reagent is used in strong sulphuric acid solution. Maximum colour development takes 1 to 3 minutes and the colour is stable for 10 to 30 minutes. The absorbance is measured at 437 mμ.

Jones and Pridham[66] have shown that the orange–yellow colour produced by heating a sugar in glacial acetic acid with benzidine can be used to determine the sugar. In this way many monosaccharides and methylated derivatives and a few disaccharides, *e.g.* sucrose, are determined.

The acceleration of the oxidation of benzidine and other amines giving colour reactions by peroxides, in the presence of various organophosphorus compounds including some nerve gases and insecticides, and of certain carboxylic acid anhydrides, *e.g.* phthalic acid anhydride, has been used in the determination of such organic compounds colorimetrically.[67] The organic substance is thought to oxidise to a peroxide which then oxidises the benzidine.

The oxidation potential of a cobaltic complex ion depends to some extent on the ligand. This makes possible the indirect determination of certain ligands colorimetrically by measuring the colour intensity on addition of a redox indicator such as benzidine or a substituted benzidine.[68] 1:2-Bis(methylthio)ethane, dibutylamine, and N:N-diethylethan-2-ol are determined in this way, but not ethylene-1:2-diamine and cyanide. The method could probably be extended to other ligands and, where the oxidation potentials of the complex ions were sufficiently far apart, selective methods devised for mixtures of two or more ligands.

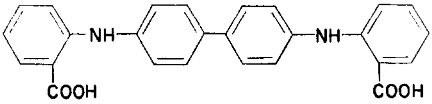
Titrimetric analysis

The period under review has produced improved procedures, new uses for existing indicators and several new indicators in redox titrimetry. Several short reviews[69,70,71] have appeared dealing with some of these developments. Various attempts have been made to study the redox properties of some indicators.

Eggertsen and Weiss[72] carried out a polarographic study of the relative oxidation potentials of benzidine and a number of substituted benzidines at pH 9·4 using a 1 : 1 water-acetone solvent mixture and a stationary platinum indicating electrode. In conjunction with absorbance measurements, they found that the amines with the lowest half-wave potentials give the highest colour intensity on oxidation and that the potentials are increased by substituents in the ring, particularly if they are electron attracting groups. Compounds with substituents ortho to the linkage between the two aromatic rings have relatively high potentials and only give slight oxidation to coloured products.[73]

Crawford and Bishop[74] studied the oxidation of *o*-dianisidine by direct potentiometric titration with cerium^{IV} and obtained formal potentials under certain experimental conditions. They discussed some of the difficulties associated with such work, the most important being the instability of the oxidised form of the reagent leading to indeterminate side reactions. Earlier, Kolthoff and Sarver[2] had commented similarly in their study of the oxidation of diphenylamine and diphenylbenzidine. The low solubility of most benzidine type compounds in aqueous systems is also a drawback, since it may delay attainment of equilibrium, which, coupled with the instability of the oxidised substance can upset the measurement of potentials.

From a study of the oxidation of N-phenyl-, and N-*o*-, N-*m*-, and N-*p*-tolylanthranilic acids, Lederer and Ward[75] showed that only the first two mentioned were of use as reversible indicators. The N-*m*-tolyl compound gives only a transient colour change and the N-*p*-compound no colour change, thus indicating that oxidation proceeds through the phenyl or tolyl nucleus *e.g.* to N:N′-di-(*o*-carboxyphenyl)-benzidine (II) from N-phenylanthranilic acid. From potentiometric studies in molar sulphuric acid, they obtained a formal oxidation potential of 1·09 *V* for N-phenylanthranilic acid, in good agreement with the value (1·08 *V*) obtained by Syrokomski and Stiepin;[76] and 1·11 *V* for N-*o*-tolylanthranilic acids. However, the actual colour changes were estimated to lie between 0·94 and 1·00 *V* and 0·81 and 1·01 *V* respectively, *i.e.* below the formal potential values in both cases.



II

It is evident from the work discussed that at present formal potentials of indicators of the benzidine and diphenylamine type are not always satisfactory, and may be of little value in the chemical systems of interest to the analyst. This will be particularly true if the indicator solubility is low and the oxidised form unstable. Efforts have been made to surmount this difficulty through the determination of the potential at which an indicator first begins to change colour visually as the oxidation potential is increased (lower transition potential) and less frequently the potential at which the colour is fully developed (upper transition potential). Such potential measurements are entirely empirical and are carried out in the redox systems in which the indicator is or might be of use. The values obtained give some indication of trends in redox potentials with change of environment *e.g.* varying acid concentration, and also give a fairly narrow potential range (*ca.* 0·15*V*) or transition interval within which the formal potential associated with the colour change of the indicator would be found under suitable experimental conditions.

Stockdale[77] compared the transition potentials of diphenylamine, N:N′-diphenylbenzidine and diphenylamine-4-sulphonic acid in the ferrous iron titration with dichromate in molar sulphuric acid. Diphenylamine and N:N′-diphenylbenzidine are considered to have the formal oxidation potential (0·76*V*) which would be expected, but Stockdale found that while the lower transition potentials are the same, the upper potentials are 0·86*V* and 0·94*V* respectively. He suggested that the higher value and hence the greater transition interval of the latter is due to its low solubility. In support, the transition intervals of a series of 3:3′-disubstituted naphthidines suggest that the lower the solubility the greater the transition interval.[52] This interval is 0·14*V* for 3:3′-dimethylnaphthidine in molar sulphuric acid but only 0·05*V* in a soluble medium consisting of equal parts by volume, of acetic and 4*M* sulphuric acids. Such results suggest that an indicator having an oxidation potential lower than required by the potential at the equivalence point in a titration may still function satisfactorily if its solubility is sufficiently low. Transition potentials for a number of indicators are recorded in Table II.

When dichromate is titrated with iron^{II} in molar sulphuric acid the equivalence point lies between 1·22*V* and 0·85*V* and in the reverse titration between 0·85*V* and 1·0*V*,[78] so that N-phenylanthranilic acid should be a satisfactory indicator in either titration, contrary to what would be expected from its formal potential, which is higher than that of ferroïn (1·06*V*). (The oxidation potential of ferroïn is generally considered to be too high for its use in the titration of iron^{II} with dichromate in molar acid). The transition interval which may be compared with the colour change pH range of an acid base indicator, could be of considerable practical value if known for redox indicators under different titration conditions.

Stockdale concluded from his study of the three indicators referred to above, that it does not make any difference to the numerical results which indicator is used, or whether phosphoric acid is present or not, in the titration of 0·1*N* solutions of iron^{II} with dichromate. The end-point, taken when maximum colour of the indicator has developed, must be reached quickly, probably to prevent irreversible oxidation and to reduce coagulation of the less soluble indicators. Irreversible oxidation of the indicator is more important in the reverse titration in which it is advisable to complete the titration without delay after addition of the indicator, particularly if diphenylamine sulphonic acid is used, as it is more susceptible than either diphenylamine or diphenylbenzidine to decomposition under such conditions.

Adams and Hammaker[79] recommended N:N′-tetramethylbenzidine and its 3-sulphonic acid derivative as indicators in the titration of iron^{II} with cerium^{IV}. Development of colour is slow, even at temperatures approaching 100° at which the oxidised forms are stable, thus promoting a tendency towards over-titration.[80] N:N′-tetraethylbenzidine is even less satisfactory for the same reason.

Uranium^{IV} is determined by titration with cerium^{IV} at room temperature using diphenylamine, diphenylbenzidine, diphenylamine-4-sulphonic acid or N-phenylanthranilic acid as internal indicator.[81] For every 50 ml of solution 3 to 5 ml of 85% orthophosphoric acid are added. By adding a large excess of phosphoric acid to complex uranium^{IV}, iron^{II} is titrated in the same solution with cerium^{IV} using

Table II. Transition potentials (in volts versus the normal hydrogen electrode at 18 or 20°) of various indicators in molar sulphuric acid.

Indicator	Transition potential, *V*		Redox system	Ref.
	Lower	Upper		
diphenylamine	0·76	0·86	A	77
diphenylamine-4-sulphonic acid	0·83	0·91	A	77,113
N:N′-diphenylbenzidine	0·76	0·94	A	77
N:N′-tetramethylbenzidine	0·86	—	B	79
N:N′-tetramethylbenzidine-3-sulphonic acid	0·88	—	B	79
naphthidine	0·79	0·83	A, B	53,113
3:3′-dimethylnaphthidine	0·71	0·85	A, B	53,113
3:3′-diethylnaphthidine	0·72	0·90	A, B	53
3:3′-di-*n*-propylnaphthidine	0·72	0·90	A, B	53
3:3′-di-*iso*-propylnaphthidine	0·75	0·91	A, B	53
3:3′-diphenylnaphthidine	0·76	0·94	A, B	53
3:3′-dimethoxynaphthidine	0·74	0·88	B	53
naphthidine-3 : 3′-disulphonic acid	0·83(a) 0·86(b)	0·91	A, B	53
3-bromobenzidine	0·90	—	A	114
3:3′-dibromobenzidine	0·94	—	A	114
N-phenylanthranilic acid	0·94	1·00	B	75
N-*o*-tolylanthranilic acid	0·81	0·11	B	75

A: Fe^{2+}–Fe^{3+} and $Cr_2O_7^{2-}$–Cr^{3+} system;
B: Fe^{2+}–Fe^{3+} and Ce^{4+}–Ce^{3+} system.
(a) $Cr_2O_7^{2-}$ as oxidant
(b) Ce^{4+} as oxidant.

diphenylamine as indicator.[82] Molybdenum^{V} and titanium^{III} are determined in the same way and will interfere in the determination of iron if present.

Gopala Rao and Sastri[83] have found that interference from oxalic acid in the determination of hydroquinone by titration with cerium^{IV} is prevented by sodium fluoride. Diphenylbenzidine and N-phenylanthranilic acid are suitable indicators. Replacement of cerium by dichromate is unsatisfactory.

Unlike most indicators of its class, N-phenylanthranilic acid is satisfactory in strong acid redox systems. As a result it has been used successfully in titrations involving vanadate as oxidant in sulphuric acid solution *e.g.* in the titration of uranium^{IV},[84] hypophosphite and phosphite.[85] Naphthidine-3:3′-disulphonic acid and probably also α-naphthylamine-β-sulphonic acid could replace phenylanthranilic acid in such titrations.

The use of a redox indicator of the benzidine type in the ferrocyanide-ferricyanide system depends on the formation of an insoluble metal ferrocyanide. Removal of the ferrocyanide from the solution raises the oxidation potential of the system. Above the transition potential the indicator will be oxidised, or reduced if the reverse procedure is used. Thus, if ferrocyanide in the presence of a little ferricyanide and a suitable redox indicator is titrated with zinc, sparingly soluble $K_2Zn_3[Fe(CN)_6]_2$ is precipitated and at the end-point all the ferrocyanide, except the small amount resulting from dissociation of the zinc salt is removed from the solution. At this point, the oxidation potential of the system increases sharply and the indicator will change colour. *o*-Dianisidine was shown to be a satisfactory indicator in this titration by Frost[86] and later by Crawford and Bishop.[73] Belcher and Nutten[87] compared naphthidine, *o*-dianisidine and *p*-ethoxychrysoïdine recommended by Tyler,[88] in this titration. They consider that naphthidine is superior to the others giving a more distinct colour change. Benzidine, 3-methylbenzidine and 3:3′-diethylbenzidine give better end-points than *p*-ethoxychrysoïdine or diphenylbenzidine, the first internal indicator used in this redox system, but inferior to *o*-dianisidine. The zinc solution to be titrated is best treated with an excess of standard ferrocyanide and the excess titrated with standard zinc solution in the presence of the indicator and a little ferricyanide. Milner[89] has shown that with naphthidine as internal indicator, suitable procedures for the determination of zinc in various non ferrous alloys and rubber ashes, can be devised. Zinc in aluminium alloys, aluminium bronzes, and white metals is separated from interfering elements by hydrogen sulphide. With tin bronzes, separation is best effected with 8-hydroxyquinoline. Zinc is separated from rubber ashes by digesting with hydrochloric acid, then making ammoniacal and filtering. Later, Belcher, Nutten and Stephen[90] found that 3:3′-dimethylnaphthidine was a more sensitive indicator and the colour more stable than the naphthidine or *o*-dianisidine colour. As good colour changes are obtained in titrations with 0·001*M* zinc solutions using this indicator as can be obtained with 0·01*M* zinc solutions using naphthidine. It is the best indicator available for the titration of very dilute solutions of metal ions with ferrocyanide. Cadmium, gallium and calcium can be titrated directly with ferrocyanide and indium by the back titration used in the zinc determination.[91] Naphthidine, *o*-dianisidine and N:N′-diphenylbenzidine are less satisfactory than 3:3′-dimethylnaphthidine in these titrations.

Brown and Hayes[92] have extended the use of 3:3′-dimethylnaphthidine by employing it with ferrocyanide and ferricyanide as the indicator system in the complexometric titration of zinc. Titration of the system containing zinc ferrocyanide and ferricyanide and indicator removes zinc from the zinc ferrocyanide precipitate, thus lowering the oxidation potential and causing the indicator colour to fade and finally discharge at the end-point. One disadvantage is that the titrant must be added very slowly near the end-point. For this reason Flaschka and Franschitz[93] recommend the addition of excess ethylenediamine-N:N′-tetra-acetic acid and back titration with zinc. In this way manganese^{II},[94] zinc, cadmium, iron^{III}, lead^{II},[93] nickel and copper[95] are determined. The titration of tin in copper alloys,[96] the rare earths,[97] and the micro titration of aluminium,[98] and gallium[99] is also possible. Benzidine has been used in such complexometric titrations[95] and it is likely that *o*-dianisidine, *o*-tolidine, naphthidine and other such indicators could also be employed.

Benzidine has been recommended as indicator in the titration of silver with iodide[100] and with bromide.[101] More recently a number of papers have appeared in which benzidine and substituted benzidines have been used in titrations of a similar nature. The indicator reaction is thought to involve both oxidation and absorption on the precipitated halide. In the methods referred to above, benzidine acetate with copper acetate and benzidine sulphate with copper nitrate were used in the titrations with bromide and iodide respectively. The colour changes are from yellow to green (bromide) and from greenish-yellow to greyish-blue (iodide). The reaction may proceed as follows (X = halide):

$$2KX + 2Cu(NO_3)_2 + BnzH_2SO_4 \rightarrow 2CuBnzX_2 + 2K_2SO_4 + 2HNO_3$$

$$2KX + 2Cu(NO_3)_2 \rightarrow CuX_2 + 2KNO_3$$

$$2CuX_2 \rightarrow Cu_2X_2 + X_2$$

The halogen produced oxidises the indicator. When precipitation is complete both the metal benzidine complex and the oxidised indicator are absorbed on the precipitate. Chloride, as expected from the reaction scheme, cannot be determined in this way, nor is this titration reversible; but with iron^{III} in place of copper^{II} it may be determined by titration with silver or used in the titration of silver in conjunction with benzidine, *o*-tolidine or *o*-dianisidine.[102] In such a system the iron^{III} may well act directly as indicator oxidant. The oxidised indicator is then adsorbed on or desorbed from the precipitate at the end-point as in the method of Lang and Messinger[103] in which chlorides and bromides are successfully titrated in 0·5*N* to 5*N* sulphuric acid solutions using diphenylbenzidine violet (oxidised diphenylamine) as adsorption indicator. Silver is titrated with iodide using gold^{III} and *o*-dianisidine as indicator in solutions up to 5·5*N* in nitric acid[104] or with iodide or bromide in the presence of a little acid using iron^{III} instead of gold^{III}.[105] The latter titration is reversible and iodide or bromide is titrated with silver ions in strong nitric acid solution.[106] The copper^{II}-*o*-tolidine system is said to be more sensitive and to give more reproducible results than copper^{II}-benzidine in the determination of silver with iodide and bromide.[107] Mercury^{I} is determined reversibly with bromide in slightly acid solution using iron^{III} and benzidine, *o*-tolidine or *o*-dianisidine as indicator.[108] For the titration of chloride or bromide with mercury^{I}, Matsuo[109] claims that the iron^{III}-*o*-dianisidine system is preferable. When a mixture of iodide and bromide is titrated with silver there are two colour changes; the first corresponds to complete precipitation of iodide and the second to bromide in 0·001*N* to 0·01*N* nitric acid solutions containing the iron^{III}-benzidine indicator system.[110] Benzidine, 3-methylbenzidine and 3:3′-diethylbenzidine have been compared in the titration of silver with bromide and iodide in the presence of copper^{II}.[111] All three indicators give sharp end-points which are superior to those obtained when conventional adsorption indicators are used as originally claimed by Sierra and Burriel. The resistance of the iron^{III}-benzidine, iron^{III}-*o*-tolidine or iron^{III}-*o*-dianisidine systems to nitric acid is greater than that of phenosafranine on silver chloride.[102] Careful control of the amount of indicator used in these titrations is necessary. Halogen and silver determinations using such oxidation-adsorption systems have been discussed by Cañavate.[106] Further comparison of these newer titrimetric procedures with established methods of analysis seems desirable in order to be able to assess them properly.

Willard and Manalo,[112] from a study of derivatives of diphenylamine as indicators in direct titrations with hypobromite, found that satisfactory end-points could be obtained with diphenylamine sulphonic acid and with 2-aminodiphenylamine-4-sulphonic acid. The former behaves reversibly but the latter which is destroyed at the end-point gives a more distinct colour change and a smaller blank value.

CONCLUSION

There may still be room for improvement of reagents of the benzidine class as precipitants and as colorimetric reagents. As a precipitant for anions, in the benzidine type molecule, a balance is necessary between the solubility of the reagent and the insolubility of the salt of the reagent to be precipitated. So far there are no data available to enable the analytical chemist to ascertain whether the best balance has already been achieved or whether further improvements are possible in the design of the most suitable reagent. Studies of a more fundamental nature on the physical and chemical phenomena involved in such precipitation reactions with available reagents, and investigation of the structure of the precipitates might assist towards this end. Benzidines and diphenylamines at present available are nearly all subject to the influence of many variables; and the colour on oxidation is either slow in developing or is insufficiently stable when developed to allow the use of these reagents in precise macro determinations. The effect of *o*- and N-methyl groups on the rate of colour development and on the stability has been studied qualitatively but little attention has been given to other groups which might be used.

In discussing indicators, several points which require investigation or re-investigation, notably in connection with the determination of oxidation potentials, have been mentioned.

Zusammenfassung—Es wird ein Überblick über die analytischen Anwendungen des Benzidins und des Diphenylamins sowie ihrer Derivate als Fällungsmittel, Nachweisreagenzien, zur kolorimetrischen Bestimmung von Oxydanzien und als Indikatoren in der Massanalyse gegeben. Es ist die Zeit von 1946 bis 1958 berücksichtigt.

Résumé—L'auteur a fait une étude des applications analytiques de la benzidine, de la diphenylamine et de leurs dérivés, comme précipitants, pour déceler et doser colorimétriquement des oxydants, et comme indicateurs dans l'analyse titrimétrique. Cette étude couvre la période: début 1946-fin 1958.

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DIREKTE KOMPLEXOMETRISCHE EISENBESTIMMUNG MIT XYLENOLORANGE ALS INDIKATOR

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Zusammenfassung—Es wurde eine komplexometrische Eisen(III)-Bestimmung ausgearbeitet, die auf einem neuen Indikationsprinzip beruht. Als Indikator wurde Xylenolorange benützt, das mit Eisen(III) einen violettblau gefärbten jedoch robusten Komplex bildet. Durch Zugabe von Eisen(II) zu der titrierten Lösung wird die übliche Verdrängungsreaktion im Endpunkte der Titration durch Redox-Vorgang ersetzt und dadurch eine sehr scharfe Indikation erzielt. Das ausgearbeitete Verfahren ermöglicht eine genaue und sehr selektive Eisen(III)-Bestimmung. Nur Wismuth, dreiwertiges Thallium und grössere Mengen von Kupfer müssen vor der Titration beseitigt werden.

DIE theoretische Grundlage der komplexometrischen Eisen(III)-Bestimmung ist durch die aussergewöhnlich hohe Stabilitätskonstante des Eisen(III)-Aethylendiamintetraacetates $K_{(\mathrm{FeY})^-} = 10^{25,1}$; vgl.[1]) gegeben. Dieser hohe Wert kann allerdings nicht voll ausgenützt werden, weil die Titration wegen der leichten Hydrolyse der Eisen(III)-Salze einerseits und der Bildung viel weniger fester Hydroxo-Komplexonate anderseits, nur auf das saure Gebiet beschränkt ist. Die untere Grenze der praktischen Anwendbarkeit der Bestimmung möge theoretisch bei pH = 1 liegen, wo die pH-abhängige Bildungskonstante ($\mathrm{K}_{(\mathrm{FeY})^-} \cdot \alpha_{\mathrm{H}}^{-1} = 10^{7,9}$),[2] etwa mit der Konstante des Bariumkomplexonates ($\mathrm{K}_{(\mathrm{BaY})^{2-}} = 10^{7,8}$) gerade noch vergleichbar ist. Für die selektive Eisenbestimmung liegen die Verhältnisse auch günstig vor, denn die Bildungskonstanten der meisten in Frage kommenden Begleitmetalle sind genügend niedriger als die des Eisens. Das gilt besonders auch für Aluminium. Obwohl jedoch die theoretischen Voraussetzungen erfüllt sind und eine ganze Reihe von komplexometrischen Verfahren für die Eisenbestimmung auch beschrieben wurde (vgl.[3]), kann dieses Problem immer noch nicht als endgültig gelöst betrachtet werden.[4] Der Grund dafür liegt in den Indikatoren.

Wie wir schon früher gezeigt haben,[2] ist die passende Empfindlichkeit des Indikators ganz allgemein nicht nur für das Gelingen der Titration, sondern auch für die Ausschaltung der Interferenz anderer Metallionen von ausschlaggebender Bedeutung. Beim Eisen ist die Situation soweit paradox, dass es kaum ein anderes Metallion gibt, das so viel Farbreaktionen wie dieses zeigt und es sehr schwer ist, unter diesen eine für die Komplexometrie in aller Hinsichtem geeignete zu finden. Einmal stimmt es mit den Farbeigenschaften oder mit der Empfindlichkeit nicht, das andere Mal sind die Komplexe des Indikators, in der Uebereinstimmung mit der ganz allgemeinen Neigung des Eisen(III) zu robust, so dass die Titration erst in der Hitze oder überhaupt nicht möglich ist. Manchmal treten noch andere Störerscheinungen zum Vorschein, wie z.B. die Oxydation des Indikators, die zu den Verlusten an Eisen(III) und dadurch zu fehlerhaften Resultaten führt. Den letztgenannten Nachteil haben ganz allgemein die o-Diphenole, bzw. Chromotropsäure und ihre Derivate, die sehr häufig und gewöhnlich in verhältnissmässig hohen Konzentrationen als Indikatoren Verwendung finden. Wie ersichtlich, ist es wünschenswert, neue und bessere Indikatoren für die komplexometrische Eisenbestimmung zu sauchen.

Wir haben schon in den ersten Mitteilungen über Xylenolorange die schöne Reaktion mit Eisen(III) teilweise beschrieben.[5,6] Die gelbe Farbe des Indikators geht in eine intensiv blauviolette über. Die Empfindlichkeit ist bei pH 1–3 in 10 ml Volumen (Makroreagenzglas) und bei der Zimmertemperatur durch das pD = 4,6 gegeben, ist also sehr hoch. Bei der erhöhten Temperatur wird sie noch gesteigert; bei 60–70°C besteht sogar in $0{,}5N$-HNO_3 immer noch das pD = 4. Bei dem Versuch, Eisen mit Hilfe dieses Indikators zu bestimmen, stellte es sich jedoch heraus, dass der Indikatorkomplex zu robust ist. Die Titration erschien selbst in der Hitze unerträglich schleppend. Deswegen wurde bisher nur die indirekte komplexometrische Eisenbestimmung mit Xylenolorange als Indikator beschrieben.[7]

Vor kurzer Zeit haben wir unserer Meinung nach eine sehr interessante Erscheinung beobachtet: Wird zu einer sauren Lösung, die Eisen(III) und Xylenolorange enthält, etwas Eisen(II)-Salz (z.B. Ferrosulfat) zugegeben, so geht die Titration mit dem Aethylendiamintetraacetat schon bei der Zimmertemperatur überraschend glatt, mit scharfem Umschlag vonstatten. Benützt man noch eine inerte Atmosphäre im Titrationskolben, werden die Ergebnisse für Eisen(III) sehr genau. Selbst ein sehr grosser Ueberschuss an Eisen(II) (z.B. 10 g Ferrosulfat in 100 ml) stört die Titration nicht. Die Bildungskonstante des Eisen(II)-Komplexonates ($K_{(\mathrm{FeY})^{2-}} = 10^{14,3}$) ist nämlich viel niedriger als die des Eisen(III), ferner reagiert der Indikator unter den erwähnten Bedingungen mit Eisen(II) nicht und seine Empfinlichkeit zu Eisen(III) passt offensichtlich gerade (vgl.[2]). Die „katalytische" Beschleunigung der Farbumschlagsreaktion durch Eisen(II) kann wie folgt verstanden werden:

Bei der Titration reiner Eisen(III)-Lösung, setzt, nachdem alles freie Eisen(III) durch Komplexon gebunden wurde (1):

$$\mathrm{Fe^{III}} + \mathrm{Y} = \mathrm{Fe^{III}Y} \qquad (1)$$

die übliche Verdrängungsreaktion (2) ein:

$$\underset{\text{blau}}{\mathrm{Fe^{III}Xo}} + \mathrm{Y} = \mathrm{Fe^{III}Y} + \underset{\text{gelb}}{\mathrm{Xo}} \qquad (2)$$

(Die elektrischen Ladungen und die Verschiedenheit der Dissoziationsformen sind hier und auch im Weiteren vernachlässigt). Wie schon erwähnt, verläuft diese Reaktion (2) zu langsam, so dass sie für die komplexometrische Eisenbestimmung unbrauchbar ist. Im Gemisch reagiert mit Komplexon sowohl Eisen(III), als auch Eisen(II) (3):

$$\mathrm{Fe^{II}} + \mathrm{Y} = \mathrm{Fe^{II}Y} \qquad (3)$$

Doch sind die Verhältnisse in jedem Augenblick der Titration durch die Gleichung (4)

$$[\mathrm{Fe^{III}Y}] : [\mathrm{Fe^{II}Y}] = [\mathrm{Fe^{III}}] \cdot K_{(\mathrm{Fe^{III}Y})} : [\mathrm{Fe^{II}}] \cdot K_{(\mathrm{Fe^{II}Y})} \text{ gegeben} \qquad (4)$$

Hieraus folgt, dass erst, dann wenn alles freie Eisen(III) gebunden ist ($[\mathrm{Fe^{III}}] \rightarrow 0$, also praktisch im Endpunkte der Eisen(III)-Titration, die Konzentration des $\mathrm{Fe^{II}Y}$ beträchtlicher ansteigen kann. Infolgedessen tritt nun die Reaktion (5) ein:

$$^{*}\underset{\text{blau}}{\mathrm{Fe^{III}}}\mathrm{Xo} + \mathrm{Fe^{II}Y} = {}^{*}\mathrm{Fe^{II}Xo} + \mathrm{Fe^{III}Y} \qquad (5)$$

Es handelt sich um eine Redox-Reaktion. Ihr Verlauf muss schnell sein, da es dabei nur zu einem Elektronenübergang kommt (die Sternchen bedeuten dasselbe Eisenatom) Der Komplex des Eisen(II) mit Xylenolorange ($Fe^{II}Xo$) ist erst um etwa pH 5 stabil. Bei niedrigerem pH, also in unserem Fall, wird er im Augenblicke seiner Entstehung gleich zersetzt (6):

$$Fe^{II}Xo = Fe^{II} + \underset{\text{gelb}}{Xo}. \qquad (6)$$

Die Indikation wird also durch die Gleichungen (5) und (6) gegeben. Zusammenfassend kann man sagen, dass durch Zugabe von Eisen(II) die langsame Verdrängungsreaktion (2) am Endpunkte der Eisen(III)-Titration durch die schnelle Redox-Reaktion (5) ersetzt wird.

Im Einklang mit unseren Vorstellungen muss die nötige Eisen(II)-Menge eine Funktion des pH sein. Tatsächlich je niedriger das pH der Lösung ist, um so mehr Eisen(II) muss benützt werden, um dieselbe Konzentration des Eisen(II)-Komplexonates und dadurch dieselbe „katalytische" Wirkung zu erzielen. Aehnliche Rolle spielt dabei die Temperatur. Bei der Titration von etwa 20 mg Eisen(III) bei pH 1,5 und bei Zimmertemperatur, ist für die Erreichung eines scharfen Farbumschlages die Menge von cca 2 g Ferrosulfat notwendig, während bei pH 3 und 60°C nur wenige mg genügen. Die Frage der Umschlagsqualität ist jedoch soweit subjektiv, dass wir uns nicht bestrebt haben, die optimale Eisen(II)-Sulfatmenge als Funktion des pH und der Temperatur wiederzugeben.

Durch Verwendung des neuen Indikationsrinzips wurde eine hochselektive Eisen(III)-Bestimmung ausgearbeitet. Von den zweiwertigen Kationen stört nur eine grössere Menge von Cu^{2+}. Von den üblichen dreiwertigen Kationen stören Bi^{3+} und Tl^{3+}; Al^{3+} stört selbst in hohen Konzentrationen bei Zimmertemperatur nicht, bei erhöhter Temperatur interferiert es hauptsächlich wegen der Reaktion mit dem Indikator (mit Komplexon verbindet es sich nur langsam), kann jedoch unter den erwähnten Bedingungen schon durch die äquimolekulare Fluoridmenge ohne Niederschlagbildung getarnt werden. Von den in Frage kommenden vierwertigen Kationen stört Ti^{4+} überhaupt nicht, die Interferenz von Zr^{4+} kann wieder mit Fluorid beseitigt werden (wenigstens dreifach molarer Ueberschuss). Das Th^{4+} wird bei pH 1–1,5 durch die aus dem Ferrosulfat stammenden Sulfatione maskiert.

EXPERIMENTELLER TEIL

Reagenzien

0,05*M Dinatriumsalz der Aethylendiamintetraessigsäure* (Chelaton 3; Chemapol–Prag). Die Lösung wurde gegen Bleinitrat als primärer Standard[8] eingestellt.

0,05*M*-*Fe* $(NO_3)_3$. Sein Titer wurde gravimetrisch emittelt.

$FeSO_4 \cdot 7H_2O$ in der Qualität „für Analyse". In Zeitabständen wurde die Eisen(III)-Verunreinigung mit Hilfe der unten beschriebenen Methode bestimmt.

Die Lösungen verschiedener Salze wurden aus den „für Analyse" Präparaten dargestellt und der Inhalt vorwiegend komplexometrisch kontrolliert.

Xylenolorange (Chemapol–Prag). Eine 0,5% Lösung (Haltbarkeit etwa 1 Monat).

Komplexometrische Eisenbestimmung in Gegenwart einer Reihe anderer Metalle

Die abgemessene und mit Hilfe der Salpetersäure zu pH 1–1·5 angesäuerte Probelösung wird in den Titrationskolben der Einrichtung für die Titration in inerte Atmosphäre eingegossen und einige Tropfen Xylenolorange-Lösung zugegeben, Danach wird einige Minuten ein Strom des inerten Gases (N_2, CO_2) durchgeleitet. Nachdem Sauerstoff aus dem System verdrängt wurde, werden etwa 2 g Ferrosulfat des bekannten Eisen(II)-Gehaltes zugegeben und unter ständigem Durchleiten des inerten Gases mit 0,05*M* Aethylendiamintetraacetat titriert. Die ursprünglich blauviolette Farbe der Lösung geht im Umschlagspunkte in reingelb über. Bei einer grossen Eisen (III)-Konzentration wird infolge der Eigenfarbe des Eisen(III)-Komplexonates die Lösung kurz vor dem Endpunkte orangegefärbt. Bei erhöhter Temperatur (ca 60°C) ist der Umschlag unter Verwendung der gleichen Eisen(II)-Sulfatmenge schärfer als bei der Zimmertemperatur.

Bei der Anwesenheit von Zirkonium, oder bei erhöhter Temperatur auch von Aluminium, wird vor der Titration eine genügende Menge von Ammoniumfluorid zugegeben. Dabei muss man für das richtige pH der Lösung sorgen. Dreiwertiges Thallium, Wismuth oder grössere als 10 mg-Menge von Kupfer müssen vor der Titration beseitigt werden.

Nach der Titration der ersten Probe können bei Serien-analyse die weiteren unmittelbar in die austitrierte Lösung pipettiert werden-soweit der Eisengehalt nicht allzu gross ist-und die Titrationen so lange nacheinander wiederholt werden sofern es der Inhalt des Kolbens erlaubt.

Mit Hilfe des beschriebenen Verfahrens wurde eine Reihe Eisenbestimmungen sowie in reinen Lösungen (bis 60 mg Eisen(III) in 100 ml), als auch in Gemischen mit anderen Ionen durchgeführt. In der letztgenannten Versuchsreihe wurde immer mit 20 mg Eisen(II) (in 100 ml) gearbeitet. Unter den angegebenen Bedingungen stören 10 mg Cu gerade noch nicht. Auch die Titration in Gegenwart von 40 mg Cr, 150 mg Ni, 120 mg Co, 200 mg Th, 500 mg Al 100 mg Ti, 30 mg Zr, oder 1000 mg NaH_2PO_4 (grössere Mengen wurden nicht geprüft) verlief störungsfrei. Statistische Verarbeitung der Resultate ergab die gleiche Standardabweichung ($\sigma = \pm 0{,}07$ mg Fe) für reine Lösungen wie für die Titration in Gemischen.

Summary—The complexometric determination of iron^{III}, based on a new end-point procedure, has been developed. Xylenol orange was used as the indicator. This forms a stable violet-blue complex. By the addition of iron^{II} to the titrated solution the usual displacement reaction at the end-point of the titration is replaced by a redox process which gives a very sharp end-point. The new procedure makes possible an accurate and very selective determination of iron^{III}. Only bismuth, thallium^{III} and large amounts of copper require to be removed before the titration.

Résumé—L'auteur décrit un dosage par complexométrie du fer(III), basé sur un nouveau procédé de détermination du point équivalent. On utilise comme indicateur l'orangé de xylénol qui forme un complexe violet-bleu stable. En ajoutant du fer(II) à la solution à titrer, la réaction de déplacement usuelle au point équivalent du titrage est remplacée par un processus d'oxydoréduction qui donne un point équivalent très net. Ce nouveau procédé rend possible un dosage du fer(III) précis et très sélectif. Seuls le bismuth, le thallium(III) et de grandes quantités de cuivre doivent être séparés avant le titrage.

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THE EFFECT OF ABSORBANCY UPON RAMAN INTENSITIES IN SOLUTIONS

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Summary—Reasonable agreement is obtained in the relationship between intensities of Raman lines as measured experimentally and as calculated from an equation derived on the basis of absorbancy laws. A direct relationship between Raman intensity and concentration exists with excitation outside an absorption band, and an inverse relationship over some or all concentration ranges is found with excitation within an absorption band.

THE Raman effect was predicted in 1923 and first observed in 1928. Research in Raman spectroscopy has proved very valuable in the calculation of thermodynamic data and in the interpretation of molecular structure. Raman spectra are also of considerable potential use in analytical chemistry, but the development of analytical applications has proceeded quite slowly.[1,2] Experimental difficulties have seriously limited the widespread development of analytical applications, although much has recently been accomplished in the design and construction of instruments for analytical use.

Quantitative analytical applications must be based upon the intensities of Raman lines. However, the relationship between line intensity and concentration of the Raman-active component is not necessarily linear, and this relationship may even differ from one Raman line to another for the same component. Placzek has predicted that the Raman intensity is greater if excitation occurs within an absorption band than if excitation is not within an absorption band.[3] Others have considered some of the implications of this effect.[4–6] The purpose of the present study is twofold: to investigate experimentally the influence of absorption properties upon the relationship between Raman intensity and concentration; to offer an interpretation thereof in terms of usual absorbancy laws.

EXPERIMENTAL

Raman spectra of aqueous solutions of sulphuric and phosphoric acids were obtained with specially designed apparatus[7] consisting of a helical quartz lamp with predominant 2537 Å output, a quartz sample tube placed within the helical lamp, a specially constructed mercury vapour resonance filter operated at 120°C, and an A.R.L. 1.5-meter concave grating monochromator with photographic recording of spectra. Intensity values were obtained with the aid of a Leeds and Northrup recording densitometer by conventional procedures. A Rayleigh line close to the Raman line was used as the standard in a modified internal-standard method.

Results are tabulated in terms of concentration vs. ratio of Raman to Rayleigh intensities in Table 1 for several Raman lines of sulphuric acid and in Table II for two Raman lines of phosphoric acid. For sulphuric acid it is evident that the intensity ratio rises with increasing concentration for every Raman line listed. Similar relationships were found for the Raman intensities alone, which were used in calculating the intensity ratios of Table I. For phosphoric acid the same "normal"

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relationship exists between intensity and concentration for 3131 Å excitation except for the lowest concentration listed, but with 2537 Å excitation there is a decrease in Raman intensity with increasing concentration throughout the entire concentration range.

In order to ascertain experimentally the influence of absorption properties upon the relationship between Raman intensity and concentration, it was also necessary to obtain absorbancy data on the same systems. This was done with a Beckman DU quartz prism spectrophotometer by conventional procedures. The absorbancy of sulphuric acid was very slight and was uniform throughout the spectral region of interest. The absorbancy of phosphoric acid was slight in the region involved in Raman spectra with 3131 Å excitation but was considerable in the region used with Raman excitation at 2537 Å.

Therefore the direct relationship between Raman intensity and concentration occurs outside an absorption band, as observed for sulphuric acid with all Raman lines measured, and for phosphoric acid with 3131 Å excitation; and an inverse relationship is found when excitation and emission occur within an absorption band, as for phosphoric acid with 2537 Å excitation.

TABLE I. INTENSITIES OBSERVED FOR SULPHURIC ACID WITH 2537 Å EXCITATION

Concentration, volume %	$I_{\text{Raman}} \div I_{\text{Rayleigh}}$ for stated Raman line					
	455 cm^{-1}	600 cm^{-1}	890 cm^{-1}	980 cm^{-1}	1030 cm^{-1}	1160 cm^{-1}
3	.104	.216	.117	.203	.591	.122
6	.167	.265	.219	.308	.670	.180
12	.247	.303	.346	.533	.854	.311
25	.361	.501	.499	.808	1.103	.385
50	.572	.741	.720	.854	1.360	.489
75	.845	.950	1.116	—	1.632	.802

TABLE II. INTENSITIES OBSERVED FOR PHOSPHORIC ACID

Concentration, Volume %	$I_{\text{Raman}} \div I_{\text{Rayleigh}}$ with stated conditions	
	2537 Å Excitation 880 cm^{-1} Raman line 2652 Å Rayleigh line	3131 Å Excitation 880 cm^{-1} Raman line 3341 Å Rayleigh line
12	.0998	.00760
25	.0383	.00280
51	.0209	.00482
85	.0136	.0107

INTERPRETATION

Raman excitation of a liquid can be visualised as consisting of three steps: incident light traversing the solution; interaction with the solution producing the Raman light;' Raman light traversing the solution to the monochromator entrance slit. Absorbancy phenomena are of significance in the first and third steps, so these steps may be treated mathematically by means of the Lambert-Beer law along with consideration of the geometrical arrangement of the light source and the sample. Rayleigh scattering can be visualised similarly but, for binary mixtures such as sulphuric or phosphoric acid in water, both components may participate in the second step. For peripheral excitation along the sample tube within a helical type lamp, the following equations may be derived for the Raman intensity, the Rayleigh intensity and the ratio of Raman to Rayleigh intensities (the derivations are included in reference 7).

$$\frac{I_{\mathrm{Raman}}}{I_0} = \frac{4\pi}{a_1{}^2 C_1{}^2}\,[e^{-a_1 C_1 D} + 1 - 2e^{-a_1 C_1 D/2}]\,K_1 C_2 \left[\frac{1}{a_2 C_1}\,(1 - e^{-a_2 L C_1})\right] \qquad (1)$$

$$\frac{I_{\mathrm{Rayleigh}}}{I_0} = \frac{4\pi}{a_3{}^2 C_1{}^2}\,[e^{-a_3 C D} + 1 - 2e^{-a_3 C D/2}]$$

$$[K_2 C_1 + K_3(100 - C_1)] \left[\frac{1}{a_3 C_1}\,(1 - e^{-a_3 L C_1})\right] \qquad (2)$$

$$\frac{I_{\mathrm{Raman}}}{I_{\mathrm{Rayleigh}}} = \frac{a_3{}^3}{a_1{}^2 a_2} \left[\frac{K_1 C_2}{K_2 C_1 + K_3(100 - C_1)}\right]$$

$$\left[\frac{1 + e^{-a_1 C_1 D} - 2e^{-a_1 C_1 D/2}}{1 + e^{-a_3 C_1 D} - 2e^{-a_3 C_1 D/2}}\right] \left[\frac{1 - e^{-a_2 L C_1}}{1 - e^{-a_3 L C_1}}\right] \qquad (3)$$

in which a_1 = absorbancy coefficient for Raman excitation line
a_2 = absorbancy coefficient for Raman line
a_3 = absorbancy coefficient for Rayleigh line
K_1 = constant for transition probability for Raman excitation of solute
K_2 = constant for transition probability for Raylejgh excitation of solute
K_3 = constant for transition probability for Rayleigh excitation of solvent
C_1 = concentration of solute (expressed in volume %, so that concentration of solvent = $100 - C$)
C_2 = concentration of the ionic or molecular form of the solute which gives rise to the Raman line (C_2 may or may not equal C_1)
D = diameter of sample tube
L = length of sample tube.

It is not feasible at the present time to make a complete experimental test of these equations which have been derived to show the influence of absorbancy phenomena upon the relationship between concentration and intensity. It is possible, however, by assuming reasonable values of the transition probabilities and using the measured values of the absorbancy coefficients for sulphuric and phosphoric acids, to determine whether the equations result in a direct or an inverse relationship between concentration and intensity for comparison to the trends of the experimental data of Tables I and II. This has been done (full details are included in reference 7), and close correlation is obtained. The direct relationship between concentration of sulphuric acid and intensity ratio is predicted from the equation. The inverse relation is predicted for 2537 Å excitation of phosphoric acid, and the inflection point in the Rayleigh intensity ratio at a concentration of about 30% is predicted for 3131 Å excitation of phosphoric acid. This seems to account for the peculiarities in the intensity relations found.

CONCLUSIONS

Experimental data have been obtained on the intensities of Raman lines for aqueous phosphoric and sulphuric acids. A general equation for the intensity has been derived on the basis of absorbancy laws. Reasonable agreement is obtained between calculated and experimental data. A direct relationship between Raman intensity and concentration exists with excitation outside an absorption band, and an inverse relationship over some or all concentration ranges is found with excitation within an absorption band. Thus absorbancy is a very significant factor in the relationship between concentration and Raman intensity. For straight-forward quantitative analytical applications of Raman spectroscopy, spectral regions in which the sample exhibits appreciable absorption should preferably be avoided.

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Zusammenfassung—Eine Formel zur Berechnung der Intensität von Ramanlinien aufgrund der Absorptionsgesetze wurde abgeleitet. Übereinstimmung der berechneten und gefundenen Intensitäten ist gut. Intensität und Konzentration sind proportional wenn die Anregung ausserhalb einer Absorptionsbande erfolgt, umgekehrt proportional bei Anregung innerhalb einer Absorptionsbande.

Résumé—On obtient pour la relation entre les intensités des raies Raman une concordance satisfaisante, que celles-ci soient mesurées expérimentalement ou calculées à partir d'une équation déduite des lois d'absorption. Il existe une relation directe entre intensité Raman et concentration lorsque l'excitation est extérieure à la bande d'absorption, et on observe une relation inverse pour tout ou partie du domaine de concentration lorsque l'excitation correspond à la bande d'absorption.

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A TRANSISTORIZED DROP COUNTER FOR CHROMATOGRAPHIC USE

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Summary—A completely transistorized drop counter for use in chromatography is described. The instrument is compact and reliable, and offers high versatility.

CORYN, Speecke and Hoste[1] recently described an electronic drop counter for use in ion exchange chromatography. As highly sensitive miniature photo-diodes are now currently available, a completely transistorized drop counter has been developed, offering compactness, reliability and versatility.

The wiring diagram, an exploded view of the photodiode housing and the transistor assembly are represented in Figs. 1, 2 and 3.

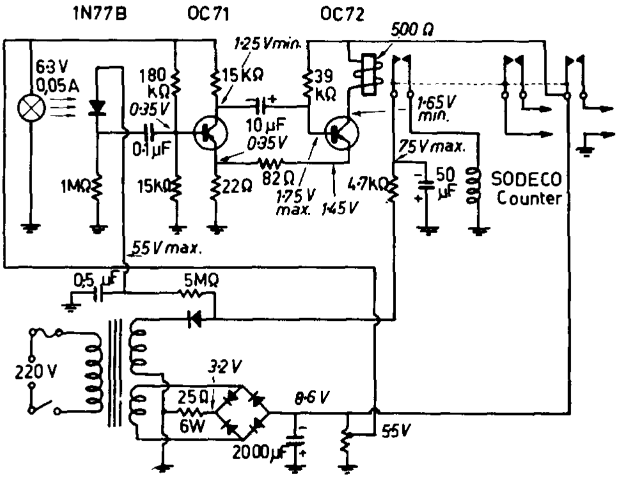

FIG. 1.

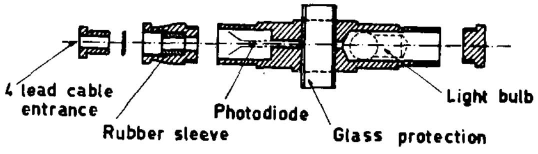

FIG. 2.

The power section of the drop counter includes the 75-volt DC high voltage, supplying the photodiode and the counter, and 8·6 volt DC for the transistors, the light source and the output pulse. The high voltage supply of the photo-diode and 5·5 volt DC of the light source are connected to

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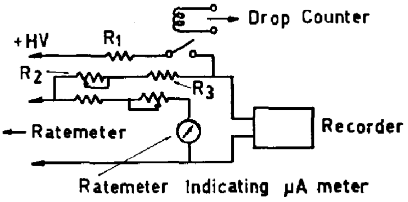
* Member of the Institut Interuniversitaire des Sciences Nucléaires.

the housing by means of a 4-lead cable, the fourth one carrying the signal. The use of ripple-free DC for the light source is required to achieve reliable operation of the counter.

When an incident light beam on the junction diode IN77B is interrupted by a falling drop, a positive 4-volt pulse is produced over the 1-Megohm load resistor and triggers the univibrator circuit (transistors OC71 and OC72). A 500-ohm relay with triple contacts is incorporated in the collector circuit of the OC72. One contact operates the Sodeco counter (type TCeZEc25), the second contact provides a negative 8·6-volt pulse to an output, whereas the third contact is connected to a second output.



R_1 : 270 KΩ 10 % 1 Watt
R_2 : 20 KΩ pot. wirewound
R_3 : 10 KΩ 5 % 1 Watt
Recorder : 5 mA 800 Ω

Fig. 4.

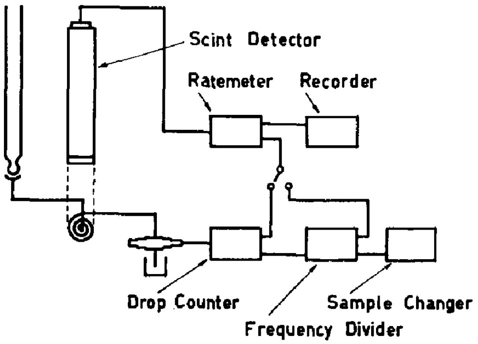


Fig. 5.

The use of a univibrator between photo-diode and counter insures high stability in operation and makes drop velocity uncritical. The counting rate however is limited by the pulse length, which is of the order of 100 milliseconds but this is adequate in most cases. No light shielding of the photodiode assembly is needed under normally occurring illuminating conditions.

In chromatography of radioactive species, the separation can be controlled by continuous monitoring of the effluent with a suitable detector coupled to a rate-meter and a recorder. The pulses of the first output from the relay are fed to the rate-meter and give a pulse for each eluted drop on the registered curve. An adequate coupling circuit for the Tracerlab Precision Rate-meter is represented in Fig. 4.

For short columns and/or species with a low value of the distribution coefficient this procedure will involve the counting of only a relatively small number of pulses on the curve to locate the eluted species. For large columns and/or species with large distribution coefficients however, this counting becomes very time consuming. Moreover the length of the paper strip becomes large, as the speed of the recorder must be high enough to distinguish between two successive pulses. This can be avoided by using the second output from the relay together with a multi-decade predetermined counter. The circuit proposed by Philips N.V.[2] with ElT tubes is adequate if preceded by a pulse shaper to trigger the multi-decade counter.

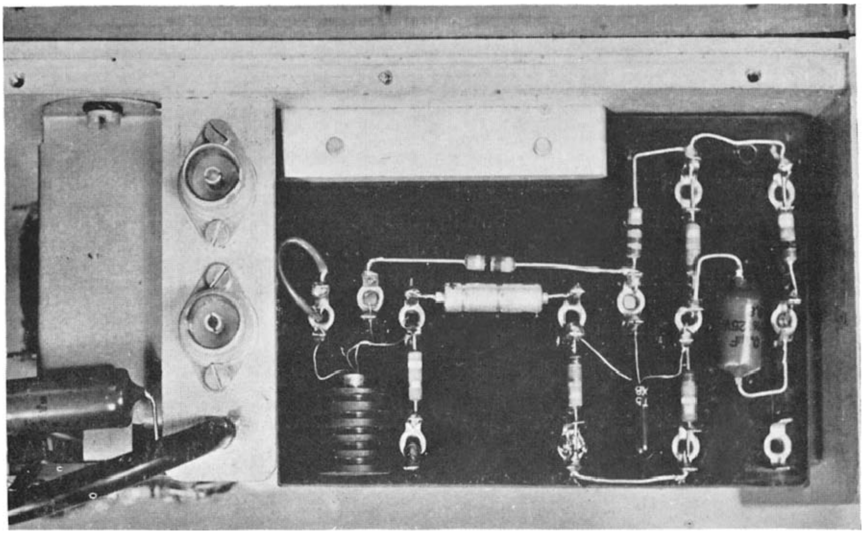


FIG. 3.—Transistor assembly

If a three-decade counter is used, any pre-set number of drops between 1 and 1000 will give rise to one pulse on the registered curve. Provision can also be made to connect the output of the decade counter to a sample changer. This allows separate collection of a preset number of drops.

A possible and highly versatile setup is represented schematically in Fig. 5.

Acknowledgement—This work is part of the research sponsored by the Institut Interuniversitaire des Sciences Nucléaires. Acknowledgements are due to L. Van de Keer for technical assistance.

Zusammenfassung—Ein zuverlässiger und vielseitig anwendbarer transistorischer Tropfenzähler für die Chromatographie wird beschrieben.

Résumé—Les auteurs décrivent un compteur de gouttes à transistors utilisable en chromatographie. L'instrument est peu volumineux, fidèle et à usages multiples.

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NEW CONTRIBUTIONS TO THE STUDY OF THE HALOGENATING EFFECT OF IODINE BROMIDE

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Summary—It was found that iodine bromide has exclusively an iodinating effect in an aqueous solution, in the presence of elementary iodine (of non interhalogen nature).

The small homolytic dissociation of iodine bromide is suppressed by iodine. In this way the formation of elementary bromine is inhibited. Consequently, in suitable conditions the brominating effect of iodine bromide is suspended.

The degree of homolytic dissociation of solutions of iodine bromide of various composition at room temperature was established.

ACCORDING to the literature,[1,2,3] iodine bromide in its substitution reactions exhibits a partial brominating effect. As part of a study of the chemistry of interhalogen compounds, a series of aromatic substitution reactions of iodine bromide was examined. It was pointed out[4] that *in an aqueous solution* (i.e. in a solvent of high dielectric constant) iodine bromide mainly behaves as an iodinating agent, and possesses brominating effect only to a subordinate extent. In the same solvent, the iodinating effect is promoted by raising the dipole character of the molecule of iodine bromide. The differences in the behaviour of iodine bromide and iodine chloride in aromatic substitution reactions were interpreted by assuming that, in addition to the heterolytic dissociation into I^+ and Br^- which predominates in an aqueous solution, a homolytic dissociation of iodine bromide into I_2 and Br_2 also takes place, owing to the appreciably weaker dipole character of its molecule. The brominating effect of iodine bromide is ascribed to elementary bromine formed during homolytic dissociation.

On studying the chemistry of bromine chloride, homolytic dissociation of a similar type was observed.[5] However, it could be suppressed by small amounts of elementary bromine or chlorine.

We believed also that the homolytic dissociation of iodine bromide can be suppressed in a similar way, by adding elementary iodine. For this purpose, solutions of iodine bromide of different iodine content were prepared and the halogenating effect of the solutions examined. Antipyrine was chosen as a reaction partner because it is known that antipyrine does not react with elementary iodine in an acid solution whilst with iodine bromide a reaction actually takes place. By suitable isolation of the reaction product, and mineralising it by fluxing with alkali, the contents of iodide and of bromide were determined.

According to our investigations, the iodine-containing solution of iodine bromide (with a content of approximately 30% of iodine) possesses exclusively an iodinating effect.

The present investigations also proved that the anomalous behaviour of iodine bromide is due to the homolytic dissociation of small extent, caused by the decreased dipole character of the molecule, and that this dissociation can be suppressed by excess iodine (or bromine).

The principle of the analytical method evolved by us[5] for the determination of the content of elementary bromine in bromine chloride could also be utilised for the determination of the content of elementary iodine in iodine bromide.

In essence, the method is as follows. The solution of iodine bromide containing elementary iodine is treated with cyanide. The reaction of iodine bromide with cyanide yields iodine cyanide and bromide ions, whilst elementary iodine reacts with cyanide during the formation of iodine cyanide and iodide ions. The iodine cyanide formed and excess cyanide are removed from the slightly acidic solution by slowly passing an inert gas (or by boiling). A quantity of iodide ions equivalent to the amount of the content of elementary iodine of non interhalogen nature* remains in the solution. This quantity can be determined by iodometry in the presence of bromide.

By this method, we determined the content of iodine of non interhalogen nature formed in the course of the homolytic dissociation, and the degree of homolytic dissociation in various solutions of iodine bromide.

According to our earlier investigations mentioned in the introduction,[4] when antipyrine reacts with a solution of iodine bromide containing bromide, 80·5% of the reaction products are iodine derivatives. On using a stoichiometric solution of iodine bromide, the amount of iodine derivatives rises to 91·3% of the halogenated products, whereas in the case of solutions of iodine bromide containing chloride, the ratio of iodine derivatives is as high as 93·7%. The various strengths in iodinating activity of the solutions mentioned were interpreted by the various degrees of the homolytic dissociation of iodine bromide.

By use of the recently evolved method, we determined the quantity of elementary iodine formed in the course of homolytic dissociation, and in this way also the degree of dissociation, in the various types of iodine bromide solutions and in a solution of iodine bromide containing elementary iodine, *i.e.* iodine of non interhalogen type (Table 1).

TABLE 1

Number	Composition of solution	Degree of homolytic dissociation %
1	0·1N IBr in 0·5N HBr	2·8
2	0·1N IBr	1·0
3	0·1N IBr in 0·5N HCl	0·5
4	0·001N IBr + 0·001N elementary I	0·0
5	0·01N IBr + 0·01N elementary Br	0·0

The figures in Table 1 confirm the results of our earlier investigations. In other words the decrease of the degree of homolytic dissociation promotes the iodinating effect of iodine bromide. In the case of a total suppression of homolytic dissociation, in the presence of excess iodine, only the halogenating effect of I^+ formed during

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* This is equal to half of the amount of elementary iodine of non interhalogen nature.

heterolytic dissociation dominates. Consequently, iodine bromide solely iodinates in this case.

EXPERIMENTAL

(1) *Iodine bromide solution;* This was prepared by the reaction

$$IO_3^- + 2I^- + 3Br^- + 6H^+ = 3IBr + 3H_2O \quad (1)$$

For a detailed description, see our earlier communications.[4,6] The hydrogen ions in equation (1) were contributed by HBr, HCl, $HClO_4$ and H_2SO_4.

(2) *Iodine bromide containing elementary iodine of non-interhalogen nature;* 10 ml of a 0·05*M* solution of iodine bromide prepared as above were made up with distilled water to about 1000 ml and mixed with 2·50 ml of a 0·1*M* solution of potassium iodide. A quantity of iodine bromide equivalent to that of iodide was reduced to elementary iodine according to the equation

$$IBr + I^- = I_2 + Br^-$$

A dilution of this order of magnitude was necessary, owing to the poor solubility of iodine. (The solution of iodine bromide prepared in this way contains 50% of elementary iodine.)

Reaction of the iodine-containing solution of iodine bromide with antipyrine

1000 ml of the solution prepared as under (2) were mixed with about 4 ml of a 1% solution of antipyrine. The reaction mixture was vigorously shaken several times, allowed to stand for 10 minutes and adjusted with sodium acetate to about pH 3. The content of iodine of the solution was back-titrated with 0·1*N* sodium thiosulphate. Then, a piece of litmus paper was put in the reaction mixture and it was made alkaline with 2*N* sodium hydroxide and shaken with 3 × 50 ml of chloroform. The chloroform solution was filtered through cotton coated with anhydrous sodium sulphate, in order to remove traces of water; the bulk of solvent was distilled off, and the residue was evaporated at room temperature. On recrystallising the product from hot water, snow-white needles resulted, m.p. 165-167°. After fluxing with potassium hydroxide, the content of both iodine and bromine were determined.

The determination of elementary iodine formed during the homolytic dissociation of iodine bromide

This was carried out similarly to the determination of elementary bromine in bromine chloride. The precise description of the technique is in our earlier communications.[5,7] In essence, excess halogen cyanide and hydrogen cyanide are removed, the solution of about 50-ml volume is acidified to pH 2 and mixed with freshly saturated chlorine water completely free of bromine, until the brownish colour caused by liberated iodine and bromine disappears and the solution turns straw-yellow (the odour of chlorine must be perceptible). On allowing the solution to stand for 10 minutes, the liquid is made alkaline by adding without any delay 10 ml of 2*N* sodium hydroxide and 2 ml of a 5% solution of potassium cyanide. After 15 minutes (this period is satisfactory for the complete hydrolysis of the formed halogen cyanides) the quantity of iodate developed during the oxidation by chlorine is measured by iodometry in the conventional way.

Zusammenfassung—Verfasser haben bewiesen, dass das Jodbrom in Gegenwart von elementarem Jod in wässriger Lösung (also in Lösung von hoher Dielektrizitätskonstante) ausschliesslich jodiert. Als Modell wurde die Reaktion Antipyrin-Jodbrom gewählt. Durch freies Jod konnte die homolytische Dissociation des Jodbroms, welche als Ursache des teilweisen Bromierungseffektes anzusehen ist vollständig zurückgedrängt werden. Es wurde ein analytisches Verfahren angegeben, mittels dessen der Grad der homolytischen Dissociation einwandfrei bestimmt werden kann.

Résumé—On a trouvé que le bromure d'iode a exclusivement un effet iodant en solution aqueuse et en présence d'iode élémentaire (de nature non "interhalogène"). La petite dissociation homolytique du bromure d'iode est supprimée par l'iode. La formation de brome élémentaire est ainsi empêchée. En conséquence, on peut supprimer, dans des conditions appropriées, l'effet bromant du bromure d'iode.

On a établi le degré de dissociation homolytique, à la température ambiante, de solutions de bromure d'iode de compositions variées.

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PRECIPITATION OF BARIUM CHROMATE FROM HOMOGENEOUS SOLUTION USING COMPLEXATION AND REPLACEMENT

A SEPARATION OF BARIUM FROM RELATIVELY LARGE AMOUNTS OF STRONTIUM AND LEAD

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Summary—A new procedure is presented that efficiently separates barium from relatively large amounts of strontium and lead. The barium is precipitated as the chromate from a solution in which the multivalent cations are complexed with EDTA. The barium ions are homogeneously released in solution when magnesium ions are slowly introduced into the solution. The magnesium ions gradually replace the barium ions from their EDTA complexes, bringing about a precipitation of barium chromate from homogeneous solution.

This slow formation of barium chromate crystals holds co-precipitation to a minimum and produces crystals that are easily filtered and washed. More than 99.7% of the barium can be precipitated as the chromate, with less than 0.6% of the strontium, when the two ions are in equal molar concentration.

THE separation of barium as the chromate in the presence of strontium has been troublesome and tedious.[1-3] Usually a double precipitation is necessary if appreciable amounts of strontium are present. Small amounts of lead interfere in all these methods. Recently Ballczo and Doppler[4] used EDTA to improve the separation. This modification has the disadvantages inherent in a conventional precipitation process.

The method described here provides an excellent separation of barium from relatively large amounts of strontium and lead using a recently developed technique involving precipitation from homogeneous solution.[5,6] This general method is based on the different stabilities of cation complexes. When insufficient complexing agent is present one cation is able to replace or "squeeze out" another cation that forms a less stable complex. By slowly introducing the cation that forms a more stable complex, the cation with the less stable complex is slowly and homogeneously released in solution.

In the case of EDTA, the barium complex is less stable than the strontium, magnesium, or the lead complex. The logarithm of the formation constants for these EDTA complexes[7] are as follows: Ba = 7.76, Sr = 8.63, Mg = 8.69, Pb = 18.0. When an excess of EDTA is added to a solution containing these four cations, they are complexed according to their respective formation constants. When chromate ions are added to the solution, a precipitate does not form because of the low concentration of free cations. A dilute solution of magnesium chloride is then slowly added to the stirred solution. Because magnesium chromate is very soluble, it does not precipitate. Instead, the magnesium ion is complexed by the excess EDTA until the excess EDTA is exhausted. At this point the magnesium ion slowly replaces or "squeezes out" the barium ion from its complex. The concentration of barium ion slowly increases until the solubility product of barium chromate is exceeded. Then precipitation of barium chromate occurs and continues slowly, for the barium ion is being released in solution at almost the same rate at which it is being removed by precipitation. The change is gradual and practically uniform, i.e. a precipitation from homogeneous solution. The crystalline barium chromate produced by this method is readily filtered, easily washed, and shows negligible co-precipitation.

EXPERIMENTAL

Procedure

Add a sample containing about 0.5 millimole of barium (about 70 milligrams) to a 600 ml beaker. Dissolve the sample in 200 ml of distilled water and add an excess of EDTA. (This must be sufficient to complex all the barium and all the cations in the solution that form an EDTA complex more stable than the barium EDTA complex. One hundred and ninety milligrams of reagent grade disodium ethylenediaminetetra-acetate dihydrate will complex 70 milligrams of barium.) Make the solution distinctly alkaline with ammonium hydroxide and add about 1.0 millimole of potassium chromate. Then adjust the solution to about pH 10 with ammonium hydroxide and the volume to about 400 ml.

Place the beaker on a hot plate and heat to about 90° to 95°. Stir the solution gently with some mechanical device and slowly add a magnesium chloride solution (about $0.02M$) by introducing one drop every 4 to 6 seconds. The amount of magnesium chloride added must be sufficient to exhaust all the free EDTA and also to replace all the barium from its EDTA complex. This means that more than 0.6 millimole of magnesium must be added. The amount of magnesium chloride can vary widely depending on the sample. (See Tables II and III). The time required to add slowly the magnesium chloride solution will be about one hour.

After all the magnesium chloride has been added, filter the hot solution through a tared Selas crucible. Wash the precipitate into the crucible using a $0.001M$ potassium dichromate solution made just alkaline with ammonium hydroxide. Finally, wash with three small portions of distilled water. Dry the precipitate of barium chromate at 110° to 120° for two hours before weighing.

Notes on procedure. The procedure followed in this experimental work is fairly flexible but in attempting to apply this technique to any specific separation problem several general conditions must be met.

The EDTA must always be in excess before the addition of chromate, otherwise barium chromate will immediately precipitate when chromate ions are added.

Enough chromate ion must be added to assure quantitative precipitation. About twice the theoretical amount of chromate is needed but four times as much has no appreciable effect on the separation. (See Table II)

Enough magnesium ion must be added to take up all the excess EDTA and also to replace all the barium from its EDTA complex. An excess of magnesium ions will not noticeably affect the results, but insufficient magnesium ions will not bring about the complete precipitation of the barium. (See Table II)

Reagents

Approximately $0.1M$ solutions of $BaCl_2$, $SrCl_2$, $MgCl_2$, $K_2Cr_2O_7$, $Pb(NO_3)_2$, $Ca(NO_3)_2$, $Fe(NO_3)_3$, and EDTA were prepared by dissolving 0.20 mole of the reagent-grade salt in distilled water and making the volume up to two litres.

Five millicuries of radioactive 140-barium, (as $BaCl_2$), and two millicuries of 90-strontium, (as $SrCl_2$), were obtained from Oak Ridge National Laboratory and diluted up to 100 ml.

Aliquots of these solutions were taken as needed.

Radiochemical measurements

Only radiochemical methods for determining traces of barium in large quantities of strontium and traces of strontium in large quantities of barium are satisfactory. Therefore the use of radioactive tracers was necessary in order to establish the efficiency of the described procedure.

About 2 to 4 microcuries of 140-barium, plus the daughter 140-lanthanum, were added to the starting solution used in each radio-chemical determination of barium in the filtrate. The 140-lanthanum presents a slight complication because it remains in the filtrate when the barium chromate is precipitated. This means that an immediate count of the filtrate would yield false results unless a complicated set of time data and formulas were used. Instead, a suitable waiting period to allow for decay of the 140-lanthanum was used.

The half-life of 140-barium is 12.8 days and the half-life of 140-lanthanum is 40 hours.[8] In 10 half-lives, or 400 hours, the 140-lanthanum in the filtrate would decay to an almost insignificant amount. Meanwhile, the 140-lanthanum in the precipitate would increase and reach radiochemical equilibrium with the parent 140-barium. A waiting period of at least two and one half weeks was required before any counting of the filtrate to precipitate ratio of "tagged" barium was done. Each sample was counted again at a later date to confirm the validity of the first ratio determination.

The same general procedure was used with the 90-strontium and its daughter 90-yttrium. About two microcuries of the mixed radioisotopes were added to each starting solution. 90-Yttrium does not precipitate with the barium chromate but remains in the filtrate.

The half-life of 90-strontium is about 20 years and the half-life of 90-yttrium is about 64 hours.[8] In about 6 half-lives the 90-yttrium will grow in the precipitate and approach a constant level. A waiting period of at least two and one half weeks was used before any counting of the filtrate to precipitate ratio of "tagged" strontium was done. Each sample was counted again at a later date to confirm the validity of the first ratio determination.

Results

The results obtained when 140-barium was used as a radioactive tracer are given in Table 1. The use of 140-barium has shown that the barium is quantitatively precipitated under varying conditions, and that the presence of strontium and lead have no appreciable effect on the quantitative precipitation of the barium.

TABLE I.—PRECIPITATION OF BARIUM CHROMATE USING 140-BARIUM AS TRACER

Barium taken is 0.5 millimole or 71.1 milligrams, 0.75 millimole of magnesium added to each solution.

K_2CrO_4, *millimoles*	EDTA, *millimoles*	Sr^{2+} or Pb^{2+}, *millimole*	*mg* of Ba found, gravimetric	*mg* difference, gravimetric	*mg* Ba in filtrate, radiometric
1.0	0.6	0	71.0	−0.1	0.08
1.0	0.6	0	71.1	0.0	0.19
1.0	1.1	0.5 Sr^{2+}	71.3	+0.2	0.11
1.0	1.1	0.5 Pb^{2+}	71.0[a]	−0.1	0.04
1.5	0.6	0	71.1	0.0	0.17
2.0	0.6	0	71.9	+0.8	0.06
2.0	1.1	0.5 Sr^{2+}	71.9	+0.8	0.06
3.0	0.6	0	71.2	+0.1	0.02
5.0	0.6	0	70.6	−0.5	0.05

[a] 0.80 millimole of magnesium added.

The 140-barium has made it possible to determine accurately how much barium stays unprecipitated. This was accomplished by determining the ratio of 140-barium in the filtrate and in the dissolved precipitate. The vexing uncertainties of small gravimetric errors were by-passed and an accurate measure of the small quantity of barium present in a large quantity of strontium was made.

The data in Table I show that a five-fold change in the chromate ion concentration does not markedly change the amount of barium left in the filtrate.

The use of 140-barium also made it possible to determine the quantity of barium that is solubilized during the washing operation. This was measured by counting the 140-barium activity of the washings. Radiochemical determinations of three different washings showed that 13, 2, and 9 micrograms of barium were solubilized during the washing operation.

The results obtained using 90-strontium as a radioactive tracer are given in Table II. The use of 90-strontium has made it possible to determine accurately the small quantities of strontium that are co-precipitated with the barium chromate. These results clearly show that this method provides an excellent separation of barium from strontium. The quantities of EDTA, potassium chromate, and magnesium chloride are not critical and can be varied quite widely with no appreciable effect on the strontium co-precipitated.

TABLE II.—PRECIPITATION OF BARIUM CHROMATE IN THE PRESENCE OF STRONTIUM USING 90-STRONTIUM AS TRACER.

Barium taken is 0.5 millimole or 71.1 milligrams

K_2CrO_4, *millimoles*	EDTA, *millimoles*	$SrCl_2$, *millimoles*	$MgCl_2$, *millimoles*	Ba found gravimetric *mg*	difference gravimetric *mg*	Sr in precipitate radiometric *mg*
1.0	0.8	0.2	0.75	70.5	−0.6	0.15
1.0	1.1	0.5	0.5	56.6[a]	−14.5	0.09
1.0	1.1	0.5	0.75	71.2	+0.1	0.17
1.0	1.1	0.5	0.75	71.1	0.0	0.25
1.0	1.1	0.5	0.75	71.2	+0.1	0.16
1.0	1.6	1.0	1.5	71.0	−0.1	0.31
1.0	2.7	2.0	1.0	71.3	+0.2	0.28
1.0	6.0	5.0	1.6	69.7[b]	−1.4	0.75
2.0	0.8	0.2	0.75	71.4	+0.3	0.18
2.0	1.1	0.5	0.75	71.1	0.0	0.16
2.0	1.1	0.5	0.75	71.4	+0.3	0.23
2.0	1.1	0.5	1.1	71.0	−0.1	0.21

[a] Insufficient magnesium chloride added.
[b] Supersaturation condition in the filtrate.

TABLE III.—PRECIPITATION OF BARIUM CHROMATE IN THE PRESENCE OF CALCIUM, LEAD, OR IRON

Barium taken is 0.5 millimole or 71.1 milligrams

Potassium chromate taken is 1.0 millimole

EDTA, *millimoles*	$Ca^{2+}Pb^{2+}$ or Fe^{3+}, *millimoles*	$MgCl_2$, *millimoles*	Ba found gravimetric *mg*	Difference gravimetric *mg*
1.1	0.5 Ca^{2+}	0.75	71.0	−0.1
1.7	1.0 Ca^{2+}	1.0	71.2	+0.1
1.1	0.5 Pb^{2+}	0.75	71.1	0.0
1.1	0.5 Pb^{2+}	0.75	71.0	−0.1
1.7	1.0 Pb^{2+}	1.0	71.1	0.0
1.1	0.5 Fe^{3+}	0.75	70.7	−0.4
1.7	1.0 Fe^{3+}	1.0	71.0	−0.1

The results obtained when equal molar and double molar quantities of calcium, lead, and iron are present are given in Table III. These data clearly show that an excellect separation of barium from calcium, lead, and iron is possible using this method. Qualitative tests were made on the barium chromate precipitates formed in solutions containing lead ions and iron ions. Neither lead nor iron were detected in these precipitates.

DISCUSSION

Precipitation is performed in basic solution for several reasons. In acid solution the oxidation of the EDTA by chromate caused discoloration of the solution and the precipitate. Furthermore, the stability of the EDTA complexes decreases with increasing acidity. At a fairly high pH, about 8 to 10, the EDTA complexes are stable and no problem of hydroxide precipitation occurs either with iron or lead. The final pH of the filtrate was still fairly high, usually between pH 8.5 and 9.0.

The heating of the solution is necessary for the production of an easily filtered precipitate. In cold solution the precipitate is powdery and also tends to stick tenaciously to the walls of the beaker.

The concentration of magnesium chloride and the drop rate were selected in order to give a reasonable time for the determination. A suitable time is needed for crystal growth, and cannot be shortened to any appreciable extent.

The experimental evidence indicates the precipitation is occurring from a homogeneous solution, even though the addition of magnesium chloride solution to the original solution automatically indicates heterogeneity. The precipitate forms in a homogeneous manner throughout the solution. Microscopic examination of the barium chromate precipitates formed using this procedure showed a uniform size and shape for the crystals. Excessive co-precipitation, characteristic of a heterogeneous precipitation, is not taking place.

An interpretation of solution conditions during the precipitation process proves interesting. The solution, just before the addition of magnesium ions, is uniform with respect to all constituents. When a drop of magnesium chloride solution is added to this original solution, the uniformity is disturbed. Compared to the solution, the portion of the liquid in the vicinity of the added drop is high in magnesium ion concentration but low in chromate ion and barium EDTA complex concentration. This decreases the chances for the immediate formation of a precipitate.

The reactions that lead to the formation of a precipitate are as follows:

$$\mathrm{BaEDTA^{2-} + Mg^{2+} = MgEDTA^{2-} + Ba^{2+}}$$

$$\mathrm{Ba^{2+} + CrO_4{}^{2-} = BaCrO_4}$$

The reactants are present in the solution in low concentration. Therefore, a definite time interval is needed for these reactions to occur. This time interval is apparently of the same order of magnitude, or greater than, the time interval needed for mixing the introduced drop. This means that conditions closely approaching uniform concentration of all constituents are reached before precipitation actually occurs.

There is no drastic fluctuation in the barium ion concentration throughout the precipitation. The barium ion concentration gradually increases as the precipitation continues, being at a maximum when the precipitation is complete.

Once the barium EDTA complex is depleted some strontium ions are released by the introduced magnesium ions. However, at this point entrapment of strontium can no longer take place, for the barium has already been precipitated.

When the magnesium ions have all been added, the strontium ion concentration is fairly high but the solubility product of strontium chromate has not been exceeded. So strontium does not precipitate.

In the solutions containing lead ions complexed by EDTA, the lead EDTA complex is not significantly affected by the addition of magnesium ions because of the great difference in stability between the lead and magnesium complexes. The magnesium complex is considerably less stable than the lead complex, and at no time during the course of the precipitation is there a significant concentration of lead ions in solution. The lead chromate solubility product constant is not exceeded at any time during the procedure and no co-precipitation of lead results even though lead chromate is more insoluble than barium chromate.

Theoretically, this method should provide a separation of barium from any cation more strongly complexed with EDTA than magnesium ion. Tables II and III show that this is true for the ions of calcium and iron as well as those of strontium and lead.

Zusammenfassung—Eine neue Methode zur Trennung von Barium von relativ grossen Mengen Strontium und Blei ist beschrieben. Das Barium wird als Chromat niedergeschlagen während die anderen multivalenten Ionen mit ÄDTA komplex gebunden sind. Das Barium wird aus dem ÄDTA-Komplex "homogen" befreit wenn man zur Testlösung Magnesiumionen zufügt. Das Magnesium verdrängt Barium langsam aus dem ADTA-Komplex.

Die langsame Bildung des Bariumchromates hält Mitfällung sehr klein und erzeugt Kristalle, die leicht zu filtrieren und waschen sind. Mehr als 99.7% barium wird gefällt unter Mitfällung von weniger als 0.6% Strontium wenn beide Ionen in äquimolarer Konzentration anwesend sind.

Résumé—L'auteur expose un nouveau procédé qui sépare avec efficacité le baryum de quantités relativement grandes de strontium et de plomb. On précipite le baryum à l'état de chromate à partir d'une solution dans laquelle les cations polyvalents sont complexés par l'EDTA. Quand on ajoute lentement des ions magnésium dans la solution, les ions baryum sont libérés d'une manière homogène. Les ions magnésium (remplacent graduellement les ions baryum dans leurs complexes avec l'EDTA, provoquant une précipitation de chromate de baryum dans la solution homogène.

Cette formation lente de cristaux de chromate de baryum maintient la précipitation à un minimum et produit des cristaux qui sont facilement filtrés et lavés. On peut précipiter plus de 99,7% de baryum à l'état de chromate avec moins de 0,6% de strontium, quand ces deux ions sont à la même concentration molaire.

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LA SEPARATION NIOBIUM-TANTALE EN MILIEU CHLORO-OXALIQUE SUR ECHANGEUR D'ANIONS

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Résumé—L'étude systématique des constantes de distribution du niobium et du tantale a permis de trouver deux éluants donnant une séparation satisfaisante sur colonne en milieu chlorooxalique sur échangeur d'anion du type Dowex 1 et 2. Le premier éluant, $0{\cdot}01M$ H_2Ox + $2M$ HCl, élue d'abord le tantale tandis qu'avec le second, $0{\cdot}5M$ H_2Ox + $1M$ HCl, l'ordre d'élution est inverse, ce qui est particulièrement important pour la détermination de traces de tantale dans le niobium et vice versa.

Les auteurs ont étudié en détail l'influence de la température, de la charge et du degré de "cross-linking" de l'échangeur.

L'expérience a démontré que la meilleure séparation est obtenue à une température de 25° pour l'éluant rapide et de 45° pour l'éluant lent. Parmis toutes les résines étudiées le Dowex 1–X8 donne lieu à la séparation la plus favorable pour les deux éluants.

INTRODUCTION

DIFFÉRENTS auteurs[1–14] ont appliqué des méthodes chromatographiques à la séparation quantitative niobium-tantale. Cette séparation est en effet très laborieuse par les méthodes classiques, due à la grande analogie des propriétés chimiques de ces éléments.

Nous nous sommes proposés d'étudier cette séparation sur échangeur d'anions en milieu chlore-oxalique afin d'éviter l'emploi de l'acide fluorhydrique[1,5–7] qui peut donner lieu à des inconvénients pratiques. L'emploi de l'acide chlorhydrique seul, tel que l'ont proposé Huffman, Iddings et Lilly,[2] semble peu indiqué, vu l'instabilité des solutions chlorhydriques de ces éléments. J. Gillis[3] c.s. avait déjà démontré que la séparation en milieu chloro-oxalique est praticable.

Cette étude a été entreprise à l'aide des traceurs radio-actifs ^{95}Nb (produit de fission) et ^{182}Ta. Seul l'emploi de traceurs radioactifs offrait en effet la possibilité d'étudier cette séparation, les méthodes classiques de la chimie analytique ne permettant pas simultanément le dosage de traces de niobium et de tantale en solution chloro-oxalique.

DETERMINATION DES CONSTANTES DE DISTRIBUTION

Les constantes de distribution K_D, telles que définies par Kraus et Moore,[15] ont été déterminées par équilibrage des traceurs radioactifs du ^{95}Nb et du ^{182}Ta dans 10 ml de solution en présence de 100 mg de Dowex 2 (50-100 mesh) à 25° ± 0·1°. La concentration en Ta était de $4 \,.\, 10^{-6}M$ tandis que le Nb était carrier free. Les traceurs sont conservés en solution d'acide oxalique à 5% afin d'éviter la formation de radio-colloides. L'expérience montre que l'équilibre entre les deux phases est très lent à s'établir et requiert au moins 6 heures.

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* Chercheur agréé de l'I.I.S.N.

Après équilibrage et filtration de la résine, l'activité de la solution est déterminée dans un échantillon de 4 ml à l'aide d'un compteur à scintillation équipé d'un cristal creux NaI(Tl). La constante de distribution se calcule d'après l'équation (1):

$$K_D = \frac{\text{Activité par g de résine}}{\text{Activité par ml de solution}} = \frac{(A_T - 10\,A)10}{A} \qquad (1)$$

A_T = activité totale introduite

A = activité par ml après équilibrage.

SEPARATION SUR COLONNE

La Fig. 1 démontre que deux éluants conviennent pour effectuer une séparation quantitative sur colonne, notamment $0{\cdot}01M$ H_2Ox + $2M$ HCl (éluant rapide) et $0{\cdot}5M$ H_2Ox + $1M$ HCl (éluant lent), le rapport des constantes de distribution β étant supérieur à 2. Quoique les éluants avec une teneur en HCl de $0{\cdot}5M$ et de $0{\cdot}25M$ HCl, donnent aussi lieu à un rapport β favorable, ils sont peu indiqués pour l'emploi sur colonne, les valeurs absolues des K_D étant trop élevées.

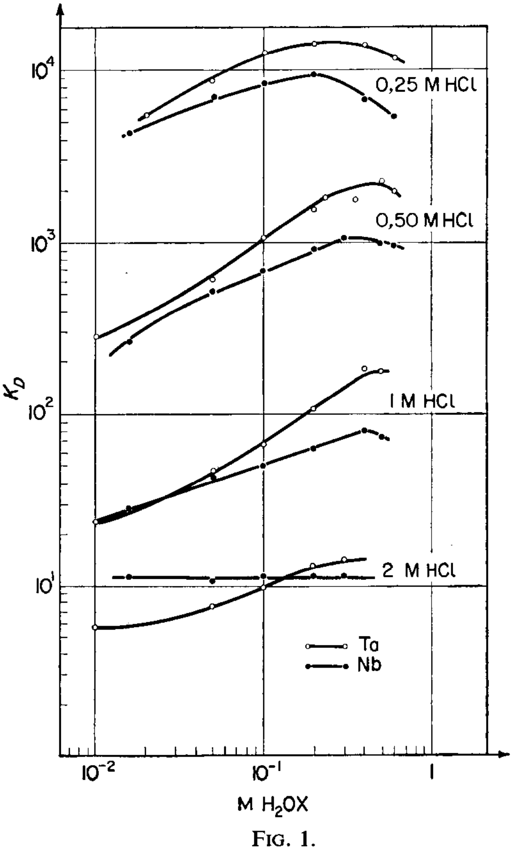


FIG. 1.

A l'aide des éluants proposés il apparait d'autre part qu'il est possible d'inverser l'ordre d'élution des deux éléments. Ceci semble particulièrement important pour la séparation de traces de tantale dans le niobium et vice versa.

Appareillage

Le schéma de l'appareillage pour contrôler la séparation sur colonne est represénté dans la Fig. 2. Il consiste essentiellement d'un tube en verre à double paroi contenant la résine, et pouvant être raccordé à un thermostat. Un rodage sphérique relie la colonne à une spirale capillaire au dessus de laquelle se place le détecteur à scintillation, raccordé à un débit-mètre et à un enregistreur.

Le volume de l'eluant est mesuré par comptage électronique des gouttes. Chaque goutte donne en outre une impulsion sur la courbe enregistrée. Pour des volumes d'élution relativement grands, le compteur permet de ne donner qu'une impulsion par 50 gouttes, ce qui facilite la détermination des volumes d'élution et permet une vitesse d'enregistrement plus faible. Le compteur de gouttes a été décrit en détail ailleurs.[16] La résine employée était le Dowex 2, 100–200 mesh, conditionné par l'éluant. La vitesse d'élution était de 0·2 ml par minute. Pour l'éluant rapide, la section de la colonne était de 0·185 cm^2 tandis que la hauteur était environ 40 cm. Pour l'éluant lent la section était de 0·255 cm^2 et la hauteur environ 7·5 cm. Pour la détermination des constantes d'élution les volumes furent corrigés pour le volume mort entre la colonne et le détecteur.

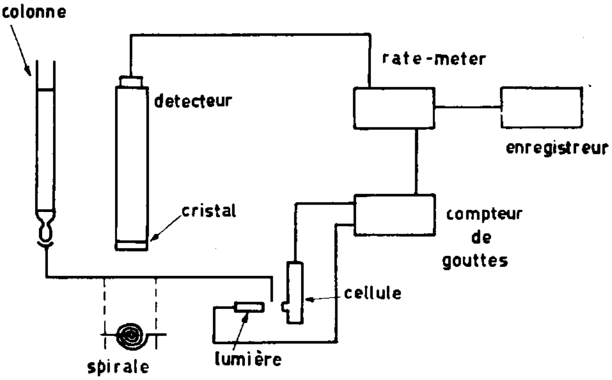


FIG. 2.

Calcul des constantes d'élution

Les constantes d'élution furent calculées d'après Kraus et Moore[1]:

$$E = \frac{dA}{V_{\max}}$$

$$E = \frac{I}{D + i}$$

$$K_D = \rho D \tag{2}$$

E = constante d'élution
d = longueur de la colonne en cm
A = section de la colonne en cm^2
$V_{\max}$ = volume où la concentration maximale est éluée
D = constante de distribution sur colonne
i = fraction de la colonne non occupée par la résine
ρ = volume de la colonne occupé par 1 g de résine.

Les constantes de distribution calculées à partir des expériences sur colonne furent trouvées en parfait accord avec les constantes de distribution déterminées par équilibrage:

éluant rapide	$\rho \cdot D_{\mathrm{Nb}} = 11{\cdot}1$	$K_{D_{\mathrm{Nb}}} = 11{\cdot}2$
	$\rho \cdot D_{\mathrm{Ta}} = 5{\cdot}0$	$K_{D_{\mathrm{Ta}}} = 5{\cdot}6$
éluant lent	$\rho \cdot D_{\mathrm{Nb}} = 74{\cdot}1$	$K_{D_{\mathrm{Nb}}} = 74{\cdot}2$
	$\rho \cdot D_{\mathrm{Ta}} = 179$	$K_{D_{\mathrm{Ta}}} = 181$

Les Fig. 3 et 4 montrent que pour les conditions expérimentales décrites ci-dessus la séparation niobium-tantale est quantitative.

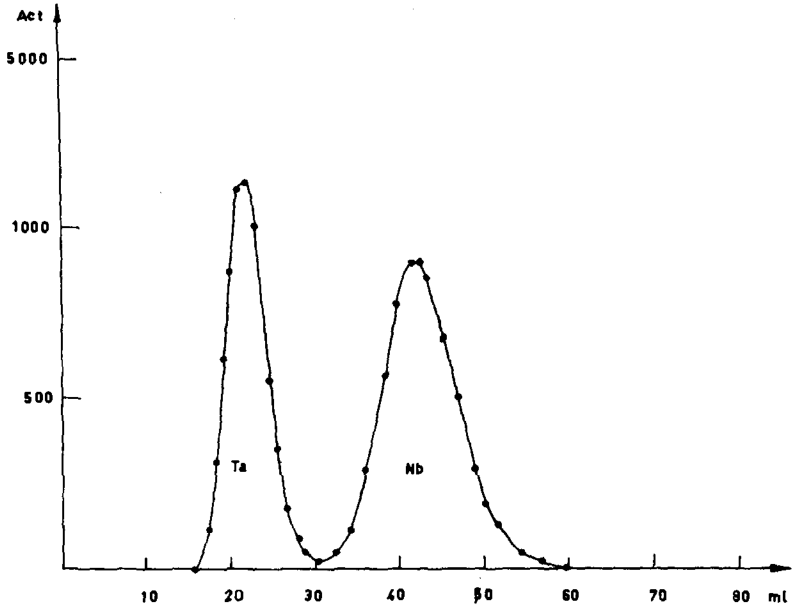
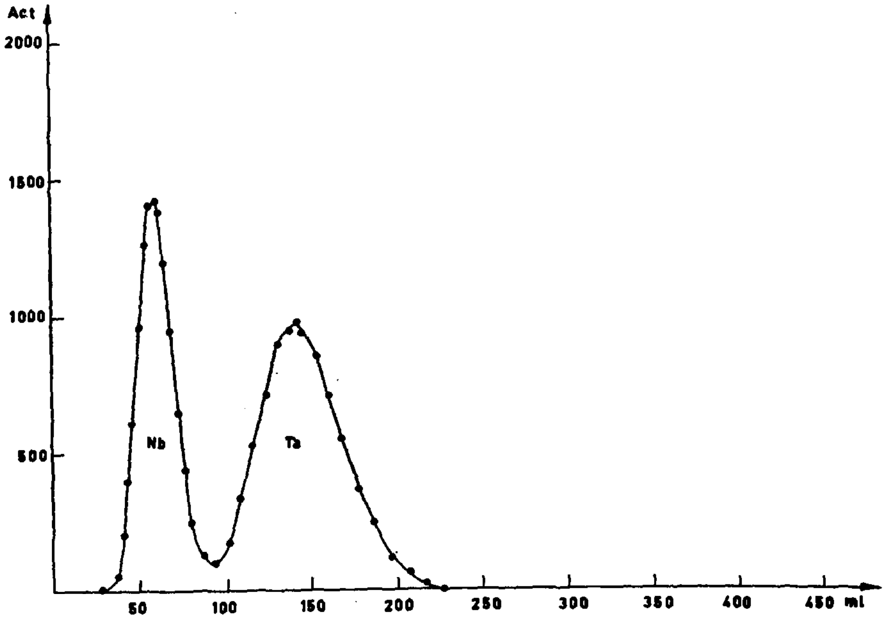

Act
5000
1000
500
Ta
Nb
10
20
30
40
50
60
70
80
ml

FIG. 3.


Act
2000
1500
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Nb
Ta
50
100
150
200
250
300
350
400
450
ml

FIG. 4.

RÉSULTATS ET DISCUSSION

Influence de la température

Pour les deux éluants mentionnés ci-dessus, la séparation niobium-tantale fut étudiée en fonction de la température, notamment de 15 à 45°. Les résultats sont résumés dans les Tableaux I et II.

Tableau I.—Influence de la température (éluant rapide).

$t°$	*d, cm*	A, *cm*^{2}	E_{Nb}	E_{Ta}	β	HEPT	
						Nb	Ta
15°	43·6	0·185	0·174	0·389	2·55	1·0	1·4
25°	43·6	0·185	0·204	0·402	1·97	0·59	0·69
35°	44·0	0·185	0·232	0·421	1·81	0·45	0·62
45°	44·6	0·185	0·257	0·457	1·78	0·41	0·58

Tableau II.—Influence de la température (éluant lent).

$t°$	*d, cm*	A, *cm*^{2}	$E_{\mathrm{Nb}} \cdot 10^2$	$E_{\mathrm{Ta}} \cdot 10^2$	β	HEPT	
						Nb	Ta
15°	7·75	0·255	3·04	1·18	2·58	0·31	0·30
25°	7·75	0·255	3·41	1·41	2·42	0·24	0·23
35°	7·75	0·255	3·60	1·56	2·31	0·18	0·16
45°	7·75	0·255	4·05	1·87	2·17	0·13	0·10

Il apparaît que pour les deux éluants le rapport β des constantes d'élution devient moins favorable à mesure que la température augmente. Les courbes d'élution montrent cependant que la séparation la plus favorable à l'aide de l'éluant rapide est obtenue à une température de 25°, tandis que la séparation la plus favorable à l'aide de l'éluant lent est obtenue à une température de 45°. Ceci est dû au fait que deux facteurs compétitifs déterminent la séparation, notamment le rapport β et la hauteur équivalente d'un plateau théorique (HEPT).

Ce dernier se laisse calculer approximativement d'après Verzele et Alderweireldt[17]

$$\text{HEPT (en cm)} = \frac{d\,B^2(K+1)}{18{\cdot}5} \tag{3}$$

où

$$B = \frac{V_{10}}{V_{\max}}$$

$$K = \frac{V_0}{V_{\max} - V_0} \cdot \frac{V_{\text{résine}}}{V_0}$$

V_{10} = volume total de toutes les fractions d'une bande éluée contenant plus de 10% de la concentration maximale.

V_0 = $d\,Ai$

Le rapport entre la constante de distribution K d'après Verzele et Alderweireldt et la constante d'élution d'après Kraus et Moore est par conséquent donné par (4):

$$K = \frac{E(1 - i)}{1 - Ei} \tag{4}$$

Comme l'ont démontré Verzele c.s.[18] le HEPT est fonction de la constante d'élution. Les valeurs HEPT calculées d'après les courbes d'élution du niobium et du tantale ne sont donc pas identiques, la différence étant surtout sensible pour l'éluant rapide.

Il apparait toutefois que les HEPT pour les deux élements se comportent de façon analogue. Dans le cas de l'éluant rapide le HEPT décroit d'environ 50% en passant de 15° à 25°, pour rester à peu près constant à partir de cette température. Il s'en suit que la meilleure séparation est obtenu à 25°. Pour l'éluant lent le HEPT décroit de manière continue de 15° à 45°, tandis que la diminution du rapport β est relativement faible. La meilleure séparation est par conséquent obtenue à une température de 45°.

Influence de la charge de la colonne

Afin d'étudier l'influence de la charge de la colonne, des quantités croissantes de niobium et de tantale furent introduite au sommet de la colonne (absorbés sur environ 50 mg de Dowex 2).

Les résultats sont résumés dans les Tableaux III et IV.

TABLEAU III.—INFLUENCE DE LA CHARGE (ÉLUANT LENT).

	Quantité introduite, *mg*	Quantité éluée, *mg*
Ta	9·8	9·4
	15·3	14·4
	28·5	27·8
Nb	14·7	13·9

TABLEAU IV.—INFLUENCE DE LA CHARGE (ÉLUANT RAPIDE).

	Quantité introduite, *mg*	Quantité éluée, *mg*
Nb	0·5	0·47
	3·0	2·84
	8·9	8·3
Ta	0·040	0·039
	0·22	0·073
	1·84	0·33
	18·1	1·63

Pour l'éluant lent l'élution du tantale et du niobium est donc pratiquement quantitative, même pour des charges relativement élevées.

Pour l'éluant rapide au contraire, l'élution du tantale n'est quantitative que pour une charge de tantale extrèmement faible, tandis que le comportement du niobium est normal. Cet éluant semble donc surtout indiqué pour séparer des traces de tantale du niobium.

Influence du pourcentage de copolymère

Plusieurs auteurs[19–21] ont démontré que le pourcentage de divinylbenzène (DVB) d'une résine du type Dowex 1 ou Dowex 2 influence fortement le pouvoir séparateur.

La résine Dowex 2 employée pour les recherches décrites ci-dessus était d'un type industriel dont le % en DVB n'était pas indiqué par le fabricant. D'après ses propriétés, il semble qu'il soit d'environ 8 %.

Il nous a semblé utile d'étudier le comportement des différents Dowex disponibles, notamment le Dowex 1–X2, –X4, –X8 et –X10 et le Dowex 2–X4, –X8 et –X10 (100–200 mesh).

Les résultats sont résumés dans le Tableau V et le Tableau VI.

TABLEAU V.—INFLUENCE DU % DVB (ÉLUANT RAPIDE).

Résine	ρ	E_{Nb}	E_{Ta}	β	HEPT		Δ (d = 40 cm)
					Nb	Ta	
Dowex 1X1	4·84	0·293	0·545	2·03	0·41	1·0	+ 2·8
X2	3·62	0·206	0·403	2·06	0·53	0·79	+ 4·5
X4	2·67	0·155	0·323	2·16	0·48	0·62	+ 8·6
X8	2·03	0·121	0·288	2·47	0·53	0·80	+14·0
X10	1·89	0·131	0·312	2·48	1·3	1·8	+ 2·4
Dowex 2X4	2·83	0·157	0·330	2·22	0·38	0·58	+ 9·6
X8	2·11	0·145	0·323	2·35	0·91	1·4	+ 4·2
X10	2·05	0·149	0·332	2·39	1·5	1·9	− 2·1

TABLEAU VI.—INFLUENCE DU % DVB (ÉLUANT LENT).

Résine	ρ	E_{Nb}	E_{Ta}	β	HEPT		Δ (d = 10 cm)
					Nb	Ta	
Dowex 1X1	4·84	0·1011	0·0649	1·56	0·25	0·28	− 9·5
X2	3·61	0·0687	0·0450	1·53	0·26	0·24	−11·3
X4	2·67	0·0375	0·0213	1·76	0·23	0·24	− 8·1
X8	2·03	0·0167	0·0076	2·36	0·17	0·20	+56·6
X10	1·89	0·0163	0·00674	2·47	0·27	0·33	+18·2
Dowex 2X4	2·83	0·0300	0·0150	2·00	0·19	0·14	+17·4
X8	2·11	0·0199	0·0086	2·34	0·24	0·23	+27·9
X10	2·05	0·0170	0·0068	2·50	0·33	0·32	+20·5

Le Tableau V montre que, pour l'éluant rapide, un pourcentage croissant en DVB améliore le facteur de séparation β qui passe de 2·03 à 2·48 pour les Dowex 1 et de 2·22 à 2·39 pour les Dowex 2. Le HEPT par contre est du même ordre de grandeur pour le Dowex 1–X1, –X2, –X4 et –X8, notamment de 0,65 cm en moyenne, pour atteindre 1·55 cm pour le Dowex 1–X10. Pour le même éluant par contre, le HEPT des résines du type Dowex 2 croît de façon continue à mesure que le % de DVB augmente.

Le Tableau VI confirme un phénomène analogue pour l'éluant lent, puisque le facteur de séparation β passe de 1·56 à 2·47 pour les Dowex 1 et de 2·00 à 2·50 pour les Dowex 2. Le calcul des HEPT démontre cependant que pour les Dowex 1, le HEPT est minimum pour le Dowex 1–X8, tandis qu'il augmente de manière continue en fonction du % de DVB, dans le cas des Dowex 2.

Il s'en suit donc que la meilleure séparation sur colonne n'est pas nécessairement obtenue à l'aide de la résine donnant le rapport des constantes de distribution le plus favorable.

Pour comparer le pouvoir séparateur des différentes résines, il est évidemment nécessaire d'employer des colonnes de longueur identique, ce qui est difficile à réaliser en pratique. A partir des valeurs expérimentales V_{max} et V_{10}, nous avons calculé les valeurs de V'_{max} et V'_{10} correspondant respectivement à une longueur de colonne de 40 cm pour l'éluant rapide et de 10 cm pour l'éluant lent.

On démontre aisément que

$$V'_{\text{max}} = V_{\text{max}} \frac{d'}{d}$$

et que

$$V'_{10} = V_{10} \sqrt{\frac{d'}{d}}$$

L'équation (3) montre que la concentration du premier élément élué n'atteint plus que 10 % de la concentration maximale, aprés avoir passé un volume de $(V'_{\text{max}_1} + \frac{1}{2} V'_{10_1})$ dans la colonne, ce qui correspond à une élution de 98·4 % du total introduit. Lorsque le volume élué atteint $(V'_{\text{max}_2} - \frac{1}{2} V'_{10_2})$ la concentration du second élément aura atteint 10 % du maximum, correspondant à 1·6 % de la quantité totale introduite du second élément.

Il est évident que la valeur

$$\Delta = (V'_{\text{max}_2} - \tfrac{1}{2} V'_{10_2}) - (V'_{\text{max}_1} + \tfrac{1}{2} V'_{10_1})$$

est un critère pour l'efficience de la séparation. Pour $\Delta = 0$, nous savons en effet que de $(V'_{\text{max}_1} + \frac{1}{2} V'_{10_1})$ ml à $(V'_{\text{max}_2} - \frac{1}{2} V'_{10_2})$, l'éluant contiendra 1.6 % du premier èlément, melange à une quantité égale du second élément. Le degré de contamination sera donc plus faible à mésure que la valeur de Δ augmente et vice versa.

Il apparait que parmi toutes les résines étudiées, la meilleure séparation est obtenu à l'aide du Dowex 1–X8, pour les deux éluants considérés.

Les auteurs remercient le Professeur Z. Eeckhaut pour de nombreux changes de vue fructueux. Les recherches décrites ci-dessus furent subsidiées par l'Union Minière du Haut Katanga et par l'Institut Interuniversitaire des Sciences Nucléaires.

Summary—The systematic study of the distribution coefficients of niobium and tantalum have allowed the discovery of two eluents giving satisfactory separation, in a hydrochloric-oxalic medium, on a column of anion-exchange resin of the type Dowex 1 or Dowex 2. The first eluent, $0{\cdot}01M$ oxalic acid + $2M$ HCl, removes the tantalum, whilst with the second ($0{\cdot}5M$ oxalic acid + $1M$ HCl) the order of elution is reversed. This is especially important in the determination of traces of tantalum in niobium and vice versa.

The authors have studied in detail the influence of temperature, and of the charge and the degree of cross-linking in the exchange resin.

Experience has shown that the best separation is obtained at a temperature of 25° with rapid elution, or 45° with slow elution. Among all the resins studied, Dowex 1–X8 gave the most favourable separation with both eluents.

Zusammenfassung—Das systematische Studium der Verteilungskoeffizienten von Niob und Tantal im Salzsäure-Oxalsäure-Medium in Anionenaustauschern vom Typ Dowex I oder 2 führte zur Elutionsmitteln, die eine zufriedenstellende Trennung gestatten. Der erste Eluent, 0,01 m Oxalsäure + 2 m HCl entfernt das Tantal, während mit dem zweiten (0,5 m Oxalsäure + 1 m HCl) die Elutionsreihenfolge umgekehrt ist. Dies ist von besonderer Wichtigkeit bei der Bestimmung von Spuren Tantal in Niob und umgekehrt.

Die Autoren haben den Einfluss der Temperature und des Vernetzungsgrades der Ionenaustauscher studiert.

Die Versuche zeigten, dass die besten Trennergebnisse bei 25°C bei rascher Elution oder bei 45° bei langsamer Elution erzielt werden. Von allen Kunstharzen gab Dowex 1-X8 die besten Trennungen mit beiden Eluenten.

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SOLVENTS FOR ULTRAVIOLET SPECTROPHOTOMETRY

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Summary—Mathematical relations are presented showing the effect of light absorption by the solvent on the absorption measurements. A simple modification in the silica-gel adsorption method of purifying *iso*octane is described that greatly improves the transmittance in the 2000 Å region. A procedure of purifying dioxan is also included.

THE ultraviolet absorption of most materials is determined by measuring the absorption of the sample dissolved in a transparent solvent. The ideal solvent is perfectly transparent through the desired spectral region, non-toxic, not too volatile, chemically inert towards the samples being examined and available at an adequate purity and at a reasonable price. Since the solvent often affects the details of the spectrum it is desirable to use a pure compound rather than a mixture so that the solvent can be clearly specified and readily duplicated.

Securing a solvent that is completely transparent through the desired spectral region is often difficult to realize. Fortunately the transmittance can be considerably less than 100% for most applications. The effects of using a solvent that has some absorption are listed below together with expressions relating the percent transmittance, T, of the solvent (for the cell length used in the measurement) to some aspect of the measurement. In deriving these relations it is assumed that the absorption measurements are made in the usual manner by comparing the absorption of a solution of the sample in one cell against the absorption of the solvent in another cell.

1. The transmittance of the solvent affects the signal to noise ratio, (S/N) and/or the slit width, W, according to the following equation in which it is assumed that the noise is proportional to the square root of the signal:

$$\frac{1}{W}\left(\frac{S}{N}\right) = k_1\sqrt{T}$$

where k_1 is a proportionality constant.

2. If the stray radiation is not significantly absorbed by the solvent, then the transmittance of the solvent affects the percentage of stray radiation, s, as follows:

$$s = \frac{k_2}{T}$$

where k_2 is a proportionality constant.

3. If there is a difference between the thickness of the sample cell and the solvent cell, any absorption by the solvent will cause an error in the absorbance measurement

according to the following expression:

$$\Delta A = (b_1 - b_2) \log \frac{100}{T}$$

where ΔA = the error in the observed absorbance

b_1, b_2 = the length in cm of the sample and solvent cells, respectively.

T = percent transmittance of the solvent in a 1-cm cell.

4. A high concentration of the sample in the solution will cause an error in the observed absorbance in accordance with the following expression:

$$\Delta A = -\frac{1}{D} \log \frac{100}{T}$$

where ΔA = the error in the observed absorbance

D = the ratio of the volume of the solution to the volume of sample.

5. A high concentration of sample in a solvent with significant absorption will also cause an error in the observed absorbance if there is sufficient interaction between the sample and the solvent to cause a change in the solvent absorption.

6. Absorbing impurities present in the solvent may react with the sample or with reagents used in preparing the solution for the measurement. Although the latter effect can be minimized by treating the portion of the solvent used in the reference cell in exactly the same manner as the solution of the sample, slight variations in the procedure can be a source of error.

The effects listed under items 1–3 do not become significant unless the transmittance of the solvent is considerably less than 100%. The first two effects are probably the most common. The magnitude of these two effects is largely dependent on the quality of the instrument being used for the measurement. Since double monochromators generally have higher resolving power and lower stray radiation than single monochromators, such instruments can tolerate a less transparent solvent.

The effects listed under items 4 and 6 can cause a significant error even if the transmittance of the solvent is only slightly less than 100%. Fortunately these conditions are seldom encountered. The condition mentioned in item 5 is also very unusual.

The above considerations show that it is impossible to set any definite specification on the transmittance of the solvent since its effect is dependent on such factors as the sharpness of the absorption peak in relation to the resolving power of the spectrophotometer, the percentage of stray radiation, the actual absorbance of the sample, the relative length of the two cells, the dilution factor and other details of the particular application.

If absorption measurements are to be made on a wide variety of samples, several different kinds of solvents must be available. The solvents most commonly used in this laboratory for ultraviolet spectrophotometry include water, methanol, chloroform, dioxan and *iso*octane. A mixture of equal parts of dioxan and *iso*octane is used more than pure dioxan in order to reduce the consumption of the more expensive dioxan. In addition, this mixture is a better solvent for some materials than either solvent alone.

Fig. 1 shows absorption curves for all of these solvents, except water, of typical quality as used in these laboratories. The source of these solvents together with the details of any purification required is described in the following sections.

SOURCE AND PREPARATION OF SOLVENTS

Water

The transmittance of ordinary distilled water in a 1-cm cell should be very close to 100% through the spectral region from 4000 Å to 1900 Å. Water is commonly used as the standard of comparison for checking the transmittance of other solvents.

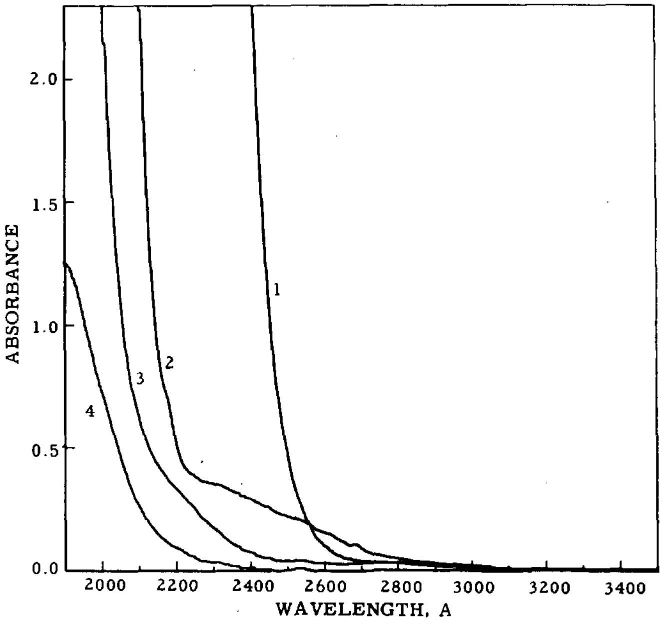

FIG. 1.—Absorption of solvents of typical quality in 1.00 cm cell.
1. Chloroform
2. Dioxan
3. Methanol
4. *iso*Octane

However, checking the transmittance of water, or of any other standard, presents a problem since this must be done on an absolute basis rather than by comparison with another material that is completely transparent. This can be accomplished by comparing the absorption spectrum of the solvent and cell to the absorption of the empty cell. If the solvent has no absorption the absorbance of the solvent and the cell should be a nearly constant amount less than the absorbance of the cell alone. Any increase in the relative absorbance of the filled cell above that observed in a region where the solvent is known to be transparent can be attributed to solvent absorption. Fig. 2 shows a check of this type on the absorption of distilled water and ordinary tap water. It will be noted that the distilled water shows no significant absorption above 2000 Å whereas the tap water shows slight absorption at 4000 Å which steadily increases at the shorter wave lengths.

Methanol

The U.S.P. grade of methanol is usually satisfactory for use in a 1-cm cell down to about 2100 Å. Although methanol is preferred because of its availability, some grades of ethanol may be satisfactory. Absolute ethanol prepared by removing the water in an azeotropic distillation with benzene is satisfactory if it does not contain too much benzene. The 3A grade of alcohol prepared by denaturing absolute ethanol with 5% of methanol may be satisfactory subject to the same limitations.

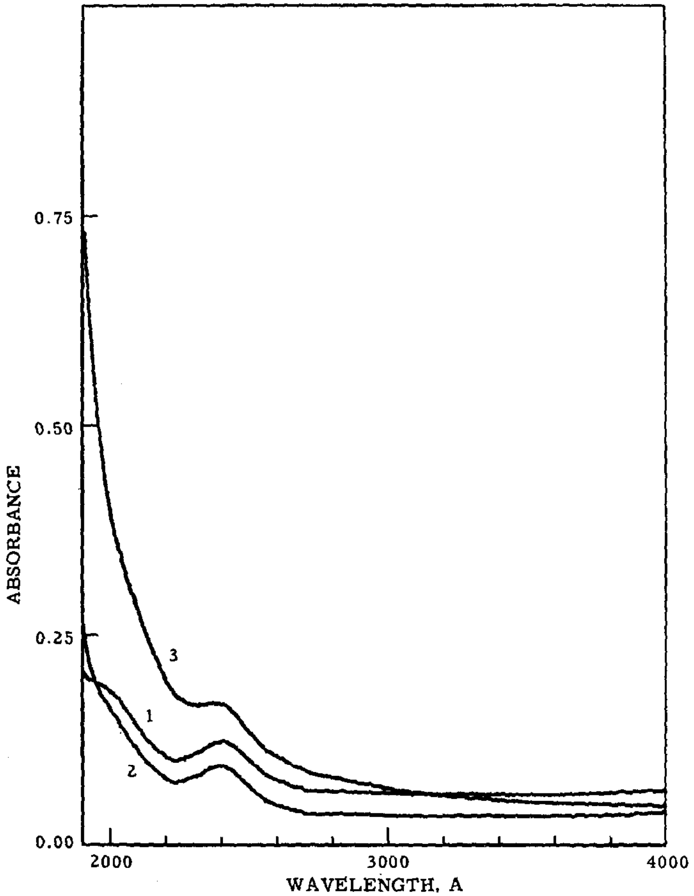

FIG. 2.—Test for a transparent solvent
1. Empty 1.00 cm cell
2. Cell filled with distilled water
3. Cell filled with tap water

Chloroform

The U.S.P. grade of chloroform is usually satisfactory down to 2500-2600 Å in a 1-cm cell without further purification.

Dioxan

Dioxan requires considerable purification before it is satisfactory for use as an ultraviolet solvent. The principal impurities affecting the ultraviolet transmittance of commercial grades are believed to be benzene, acetaldehyde, and unsaturated aldehydes. The unsaturated aldehydes are particularly objectionable since concentrations of a few parts per million considerably reduce the transmittance through a 1-cm cell. Although acetaldehyde does not have such strong absorption, it can condense and dehydrate yielding unsaturated aldehydes. The starting material for the purification described below has been a technical grade of dioxan obtained from Carbide and Carbon Company. The unsaturated impurities are removed by refluxing with aqueous alkaline permanganate. After the reaction is complete the water is salted out with sodium hydroxide and the dioxan distilled. A 20-plate distillation column has been found to be quite adequate for the distillation. This is operated at a 20 to 1 reflux ratio until the lower boiling impurities have been eliminated and then the reflux ratio reduced to 10 to 1 or 5 to 1 for the balance of the distillation.

Purification procedure

Place the dioxan in a distillation flask equipped with a reflux condenser and a means of regulating the addition of the alkaline permanganate. Heat the dioxan until refluxing commences and then start adding the permanganate reagent which contains 40 g of sodium hydroxide and 60 g of potassium permanganate per litre of water. Add the reagent fairly rapidly but not so fast that the mixture is cooled so much that the dioxan stops boiling (too low a temperature will permit the concentration of unreacted permanganate to build up and this will cause a very vigorous reaction if the temperature is increased). Add a volume of the alkaline permanganate equal to one-half of the volume of dioxan being treated. Reflux for 15 min after the addition of the last of the reagent and then cool to room temperature.

Decant the dioxan off from the bulk of the manganese dioxide (or filter) and then saturate with sodium hydroxide. Separate the dioxan layer and charge to the distillation column with a little solid sodium hydroxide and distil. The first cuts from the distillation will contain the benzene and the residual water in the form of a dioxan-water azeotrope boiling at 88°. Examine the ultraviolet absorption spectra of the cuts obtained on the dioxan flat and save all those which show a satisfactory transmittance. Most of the cuts obtained after elimination of the benzene should be suitable for use as an ultraviolet solvent. Store the purified dioxan under an inert atmosphere in order to reduce the rate of peroxide formation. A distillation from solid sodium hydroxide will clean up material that has deteriorated through air oxidation.

iso*Octane*

*iso*Octane is commercially available in a specially purified grade for use as an ultraviolet solvent. Since this grade is rather expensive, it is more economical to purify a cheaper grade whenever considerable solvent is required. The ASTM, Knock Test Reference Fuel *iso*octane sold by Phillips Petroleum Company is a satisfactory and relatively inexpensive starting material. A simple percolation through silica gel is satisfactory for use in a 1-cm cell down to about 2150 Å. However, residual traces (probably less than 0.1 %) of highly branched olefin cause considerable absorption at shorter wavelengths. These low concentrations of olefins are not readily removed by a simple treatment with silica gel. However a combination of a simple chemical treatment and a silica-gel percolation is quite effective. The chemical treatment is based on the reaction of nitrogen tetroxide with olefins[1] to form nitrosates which are adsorbed on silica gel. The excess nitrogen tetroxide is preferably removed by treatment with some alkaline reagent such as Ascarite prior to the silica gel treatment. The usual practice is to prepare two 1-gallon batches at

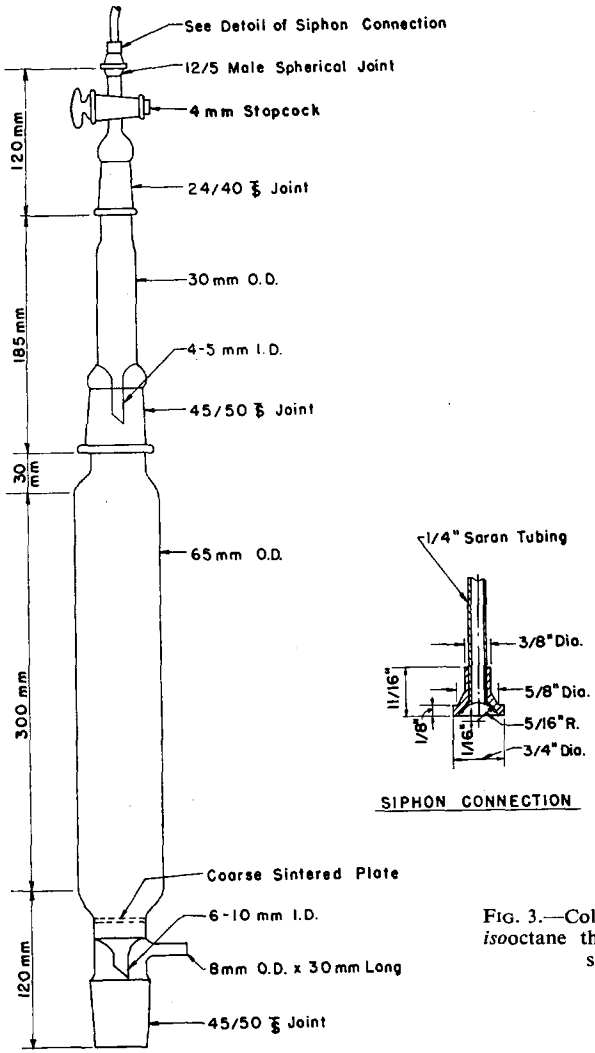

FIG. 3.—Column for percolating *iso*octane through ascarite and silica-gel.

the same time. The adsorption column used for the purification is shown in Fig. 3. It is identical to the column described previously[2] for treating *iso*octane except that a small tube for Ascarite has been added to the top.

Purification procedure

Prepare the nitrogen tetroxide required for the treatment ahead of time by sealing 2 g (1.4 ml) in each of a series of glass tubes. To accomplish this, first condense nitrogen tetroxide vapour from a cylinder in a cold trap immersed in ice water. (Tygon tubing can be used for connecting the cold trap to the cylinder). Then pour the desired quantity of liquid into 8-mm I.D. × 30-cm long glass tubes, also immersed in ice, and seal off the upper end. Store the sealed tubes in a cold chest at a temperature at which the nitrogen tetroxide solidifies in order to reduce danger of accidental loss when the tube is broken open. Pour the entire contents of one of the nitrogen tetroxide tubes into each gallon of the Phillips *iso*octane specified previously.

Charge the small upper tube of the silica-gel column with approximately 60 g of Ascarite and the lower tube with about 500 g of 28-200 mesh silica gel. (This charge is adequate to treat two gallons of *iso*octane.)

Allow the *iso*octane-nitrogen tetroxide mixture to stand for at least 30 minutes and then syphon the solution into the top of the column of Ascarite and silica gel.

The effluent from the column is ready for use. It should be satisfactory down to about 2100 Å in a 1-cm cell and to about 1900 Å in a 0.1-cm cell. The analytical method for determining olefins[1] upon which this procedure is based, recommends cooling the material in ice before adding the nitrogen tetroxide in order to avoid any danger of too vigorous a reaction. Although this precaution seems unnecessary in this instance where the olefin concentration is very low, this procedure should be applied with caution to the treatment of other materials that may be more reactive.

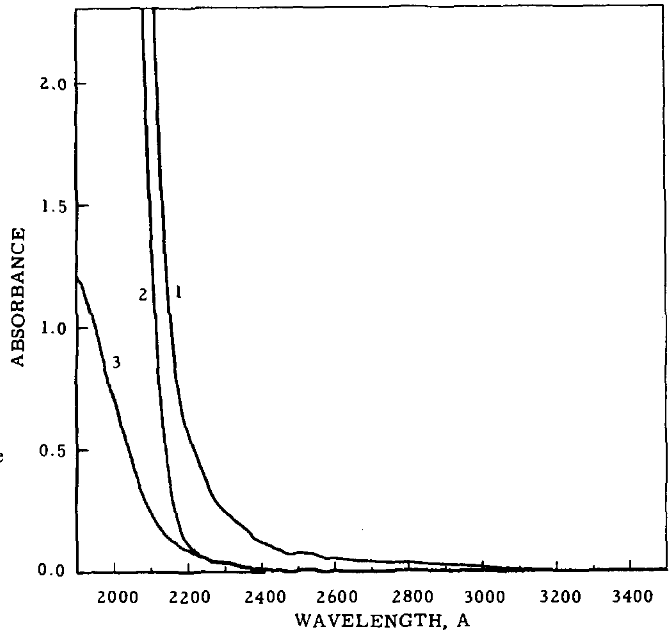

FIG. 4.—Purification of *iso*octane Absorption in 1.00 cm cell vs. distilled water

1. Original *iso*octane
2. Product from silica-gel treatment
3. Product from N_2O_4 plus silica-gel treatment

Fig. 4 shows the relative absorption of the original unpurified *iso*octane and the products obtained by silica gel treatment only and by treatment with nitrogen tetroxide, Ascarite and silica gel.

Zusammenfassung—Mathematische Berechnungen zeigen den Einfluss des Lösungsmittels auf die Lichtabsorption bei Absorptionsmessungen. Eine einfache Modifikation der Silikagelmethode zur Reinigung von Iso-Octan, welche eine Verbesserung der Durchlässigkeit bei 2000 Å zeigt, wird beschrieben, ebenso ein Verfahren zum Reinigen von Dioxan.

Résumé—L'auteur présente des relations mathématiques montrant l'effet de l'absorption de la lumière par le solvant sur les mesures d'absorption. Il décrit une modification simple de la méthode d'adsorption par le silica-gel pour la purifications de l'*iso*-octane, ce qui améliore beaucoup la transmission dans la région de 2000 Å. Le mémoire comprend aussi un procédé de purification du dioxane.

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THE FORMAL OXIDATION POTENTIALS OF SUBSTITUTED 1:10—PHENANTHROLINE FERROUS COMPLEXES OF LOW SOLUBILITY

THE PREPARATION AND REDOX POTENTIALS OF THE VANADATE-VANADYL SYSTEM OF POTENTIOPOISED SOLUTIONS

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Summary—The preparation of oxidation potentiopoised reference solutions is described. The oxidation potentials provided are stepwise in augmented values over the range 0.9 to 1.23 volt. The vanadate-vanadyl system is employed. The magnitude is dependent upon the increase in sulphuric acid formality over the range 0.1 to 6.0 formal. These solutions are of the potential buffered type. Their use in the determination of redox potential of a series of the ferrous complexes of a series of substituted 1:10-phenanthrolines is described. The accuracy attained is of the order 3% or less, compared to standard values following the potentiometric titration procedures. The determinations are outstanding in rapidity.

INTRODUCTION

MANY of the available and previously investigated ferrous complex anions formed by substituted 1:10-phenanthrolines are of low solubility in acid aqueous solvents. This fact does not inhibit their use as redox indicators. Solutions of 10^{-5} or less in indicator concentration are of sufficient colour intensity to serve. The usual potentiometric determination of their oxidation potential, even on a micro-analytical scale, is not without difficulty. Attaining of equilibrium potentials only at unreasonable time intervals at equivalence points is unavoidable. Their oxidation potentials are closely related to the pK_a of the nitrogens of their functional group. This is an added observation of theoretical interest to be substantiated. Other colligative property relationships as a function of the nature and position of substitution in the parent ligand are associated with the oxidation potential.

The application of the principle of the use of potentiopoised reference solutions for determination of redox potentials is thought to be new. It is rapid, adequately precise by comparison with the use of conventional methods of potentiometric evaluation, and economical in reagent consumption.

EXPERIMENTAL

Preparation of potentiopoised solutions and 1:10-phenanthroline ferrous complexes

The vanadate-vanadyl couple is pH dependent. The values range from 0.9 to 1.25 volts in 0.1 to 6.0 formal sulphuric acid. The increase in potential is linear between 0.5 to 6.0 formal acid concentration. Equi-molecular vanadate-vanadyl potentiopoised solutions were prepared as follows:

1. Eighteen grams of vanadyl chloride was dissolved in 360 ml of 0.5*F* sulphuric acid. 100 ml of this solution were transferred to a 250-ml volumetric flask. An equal portion was treated by addition of excess ammonium persulfate to oxidize V^{IV} to V^{V}. Excess oxidant was removed by boiling. The vanadate solution was then added to the vanadyl solution. The flask contents were then diluted to volume with 0.5*F* sulphuric acid. This solution was 0.14*F* in both V^{V} and V^{IV} and 0.5*F* in sulphuric acid. Five-ml portions of this solution were diluted with water and requisite sulphuric acid to make 500-ml volume. This solution was 0.1*F* in sulphuric acid and 0.0014*F* in vanadate and vanadyl ions.

A series of similarly prepared solutions of 0.10*F* to 6.00*F* in sulphuric acid, and 0.0014*F* in vanadate-vanadyl ions with gradual increase in acid formality in 25 steps were prepared. Such solutions bear but a faint tinge of colour. Equal concentration of the vanadium ions provided maximum potentiopoised capacity.

2. A weighed amount of Mohr's salt was dissolved in 0.0005*F* sulphuric acid to result in a 0.0023*F* ferrous ion concentration.
3. Solutions of complexing ligands (0.010*F*) in 95% ethanol were prepared.
4. The solutions 2 and 3 were mixed in equal 5-ml portions. The resulting ligand-ferrous complex solutions were 0.0012*F* and contained approximately 40% excess ligand.

TABLE I.—FORMAL POTENTIALS OF THE POTENTIOPOISED SOLUTIONS

H_2SO_4, *F*	E_0', *volts*	H_2SO_4, *F*	E_0', *volts*
0.10	0.910	3.0	1.103
0.30	0.934	3.3	1.110
0.40	0.940	3.5	1.120
0.50	0.975	3.8	1.132
0.75	0.993	4.0	1.143
1.0	1.008	4.3	1.160
1.3	1.018	4 5	1.182
1.5	1.030	4.8	1.189
1.8	1.047	5.0	1.193
2.0	1.056	5.3	1.206
2.3	1.072	5.5	1.211
2.5	1.089	6.0	1.226
2.8	1.095		

Determination of formal potentials of potentiopoised solutions

A. Leeds and Northrup student potentiometer and a platinum-saturated calomel electrode pair was employed. Approximately 40 ml of the potentiopoised solutions in 50-ml beakers served to determine their E.M F to the nearest millivolt Steady potentials were attained after 10 minutes. Duplicate values of the formal potentials (E_0') agreed in value within ±0.003 volt. The results are found in Table 1.

By graphical inspection, the values of Table I show a linear relationship between 0.5*F* and 6.0*F* sulphuric acid concentration, or an increase of 0.047 volt for each increase of one unit in formality.

Redox potential determination employing potentiopoised solutions

Ten-millilitre portions of the potentiopoised solutions were placed in 18- by 150-mm test tubes in the order of their increasing potential. Two drops of the 0.0012*F* ferrous complex to be tested were added to each of six consecutive solutions which were thoroughly mixed. One minute after the ferrous complex had been added, the colour remaining was recorded. The transition oxidation potential upon successive additions was observed. This was taken as the potential of the potentiopoised solution which effected a complete colour change of the complex. The value selected was established by interpolation between the solution in which the colour change was first complete and the next lower solution potential in which the colour of the reduced form of the complex was barely perceptible. A mid-point interpolation was made to establish E' values.

The point of visible colour change (red to very faint blue) corresponds to 90% oxidation. By using the expression $E_0' = E' - 0.6$ volt, the formal oxidation potential at a given sulphuric acid concentration was determined.

For the purpose of showing the adequacy of the procedure the method was applied to the ferrous complexes of 1:10-phenanthroline and its 5-nitro- and 5-methyl-substitution derivatives as well as to 2:2′-dipyridine. The formal oxidation potentials of the ferrous complexes of these four products have been previously determined by other procedures.[1] The results are given in Table II.

TABLE II.—A COMPARISON OF POTENTIOPOISED REFERENCE SOLUTION DETERMINATION OF REDOX POTENTIALS WITH PREVIOUS ACCEPTED VALUES

Iron^{II} complex of	Potentiopoised colorimetric		Literature reference values		Reference
	Acid formality, H_2SO_4	E_0' (volts)	Acid formality, H_2SO_4	E_0' (volts)	
1:10-Phenanthroline	2.2	1.00	2.0	1.03	(1)
	—	—	3.0	1.02	(1)
5-Methyl-derivative	1.6	0.98	1.0	1.02	(1)
	—	—	2.0	1.00	(1)
5-Nitro-derivative	5.4	1.15	4.0	1.12	(1)
	—	—	6.0	1.12	(1)
2:2′-Dipyridine	1.4	0.96	1.0	0.97	(1)
	—	—	4.0	0.92	(1)

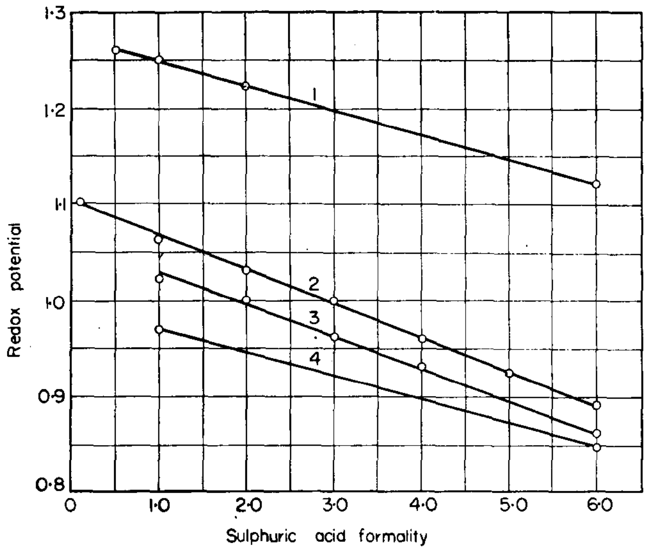

FIG. 1.—(1) 5-Nitro-1:10-phenanthroline-Fe^{II} ion.
(2) 1:10-Phenanthroline-Fe^{II} ion.
(3) 5-Methyl-1:10-phenanthroline-Fe^{II} ion.
(4) 2:2′-Dipyridyl-Fe^{II} ion.

The values of Table II show an agreement of from 0.00 volt to 0.03 volt between the exact values and those given graphically in Fig. 1. Such concordance is quite sufficient in utility for practical application. By reference to Fig. 1 the alteration in oxidation potential is seen to be linear with alteration in acid formality between 0.50 and 6.0. For the four reference standards the chief disadvantage of the procedure of the potentiopoised solution colorimetric estimation of redox potentials is its dependence upon the use of a particular acid formality. This limitation may be discounted provided the results given in Fig. 1 are assumed to be applicable in linearity over a wide range of acid formality as applied to other ferrous-1:10-phenanthrolines under consideration.

The concentration of the iron^{II} complexes in the potentiopoised solutions was approximately 10^{-5} formal. Even at this relatively low concentration a distinct colour (and hence colour change) was perceptible because of their large molecular extinction coefficients in absorption.

The formal oxidation potentials of 24 *substituted* 1:10-*Phenanthrolines*

The formal oxidation potentials of these phenanthrolines as their ferrous complexes were estimated using the above described procedure. The results are given in Table III. No difficulty was experienced in obtaining reproducible and duplicating results.

TABLE III.—COLORIMETRIC FORMAL OXIDATION POTENTIALS OF THE Fe^{II} COMPLEXES OF PREVIOUSLY UNDETERMINED 1:10-PHENANTHROLINES

1:10-Phenanthroline derivative	H_2SO_4 formality	E_0', volts	1:10-Phenanthroline derivative	H_2SO_4 formality	E_0', volts
5-fluoro-	3.2	1.05	3:7-dimethyl-	1.4	0.96
3-chloro-	4.4	1.11	3:8-dibromo-	5.4	1.21
3-phenyl-	2.4	1.02	4:7-dimethoxy-	0.1	0.85
3-ethyl-	2.1	1.00	4:7-diethyl-	0.9	0.94
4-bromo-	2.9	1.04	4:7-diphenoxy-	2.9	1.04
4-phenyl-	1.9	0.99	4:7-diphenyl-	4.6	1.13
4-ethyl-	1.4	0.96	4:6-diphenyl-	4.5	1.12
4-*n*-propyl-	1.4	0.96	5:6-*cyclo*hexeno-	1.4	0.96
3:4-*cyclo*penteno-	1.4	0.96	5:6-diethyl-	1.6	0.98
3:4-*cyclo*hexeno-	0.9	0.94	5:6-dimethoxy-	2.4	1.02
3:4-*cyclo*octeno-	1.0	0.95	5:6-dichloro-	4:4	1.11
(3:4)(7:8)-di*cyclo*hexeno-	0.3	0.87	3:5:6-trimethyl-	1.0	0.95

GENERAL CONSIDERATIONS

The formal oxidation potentials of a large number of methyl substituted 1:10-phenanthrolines as their Fe^{II} complexes have been previously determined.[1] In all cases alterations in the determined values were additive and could be predicted with accuracy. A methyl substitution in the 4 or 7 position lowers the redox potential by a value 0.11 volt. The methyl group in the 3 or 8 position lowers the value 0.03 volt when compared with the unsubstituted ligand's Fe^{II} complex. A methyl group in the 5 or 6 position lowers the value by 0.04 volt.

These observations serve to validate some of the results of Table III. Thus it would be predicted that the Fe^{II} complex of the 3:5:6-trimethyl-1:10-phenanthroline would have the redox potential of 0.95 volt in formal sulphuric acid. By determination as above described the same value was found. For the 3:7-dimethyl complex the value found colorimetrically was 0.95 volt compared to 0.92 by calculation using the known value of the 1:10-phenanthroline ferrous complex as reference. The agreement to within a maximum deviation of 0.03 volt serves to define the limitations of the presently described procedure.

Relationship of redox potential of the ligand-Fe^{II} *complex to the* pK_a *value of the nitrogens of the ligand functional group*

If the stability constants of both the Fe^{II} and Fe^{III} complexes of a series of 1:10-phenanthrolines substituted in the same position are linearly dependent upon the basicity of the chelate ligand, then the formal oxidation potentials of the ferrous complexes should show linear relationship with the pK_a values of the ligands. This relationship has been demonstrated for the ferrous-phenanthroline complexes with nitro, methyl, bromo, or phenyl substitutents in the 5 position.

Using the known rate of diminution in the formal oxidation potential of the ferrous complex of 1:10-phenanthroline as a correction factor, the colorimetric formal oxidation potentials of the complexes in 1.0*F* sulphuric acid were estimated by applying the correction. These together with the pK_a value of the ligands are summarized in Table IV.

TABLE IV.—COLORIMETRIC FORMAL POTENTIALS RELATIVE TO LIGAND pK_a VALUES

Reference 4-number	1:10-Phenanthroline derivative	pK_a‡	Fe^{II} complex E_0' in $1.0F$ H_2SO_4
(9)	4:7-dimethoxy-	6.45	0.82
(6)	(3:4)(7:8)-di*cyclo*hexeno-	6.25	0.85
(6)	3:4-*cyclo*penteno-	5.78	0.97
(6)	3:4-*cyclo*octeno-	5.66	0.94
(7)	4:7-diethyl-	5.60	0.94
(1)	3:7-dimethyl-	5.57	0.97
(8)	4-*n*-propyl-	5.45	0.97
(7)	4-ethyl-	5.44	0.97
(9)	4:7-diphenoxy-	5.34	1.10
(1)	3:5:6-trimethyl-	5.34	0.95
(6)	5:6-*cyclo*hexeno-	5.30	0.97
—	5-methyl-	5.23†	0.99(1.02)*
(7)	3-ethyl-	4.98	1.03
(3)	4-phenyl-	4.90	1.02
—	1:10-phenanthroline	4.86	1.09(1.06)*
(3)	4:7-diphenyl-	4.84	1.24
(5)	3-phenyl-	4.82	1.06
(3)	4:6-diphenyl	4.69	1.23
(9)	5:6-dimethoxy-	4.42	1.06
(2)	4-bromo-	4.03	1.10
(4)	3-chloro-	3.99	1.21
(2)	3:8-dibromo-	3.90	1.28
—	5-nitro-	3.57†	1.28(1.25)*
(4)	5:6-dichloro-	3.47	1.21
(8)	5-fluoro-	—	1.12
(6)	3:4-*cyclo*octeno-	—	0.95
(7)	5:6-diethyl-	—	1.00

* Potentiometrically determined value. Ref. (1).
† Values of reference (2)
‡ Reference (3)

The results in Table IV indicate a direct relationship between ligand pK_a and the formal oxidation potential of its ferrous complex. Although the change is not linear the formal oxidation potentials of the complexes increase as the pK_a values decrease.

It is quite evident from the results in Table IV that the formal potentials for the complexes of 4:7-diphenoxy, 4:7-diphenyl and 4:6-diphenyl derivatives are not consistent with the potentials of the others in their pK_a value relationships. In all 3 cases the inconsistency amounts to approximately 0.15 volt.

It is probable that this apparent over-potential may be due to sluggishness in reaction kinetics for the oxidation of iron by the vanadium^{V} of the potentiopoised solutions. Since the dissociation of the Fe^{II} complexes and the rate of electron exchange with iron are very slight, the reaction mechanism probably involves electron transfer through the aromatic rings. Large substituent groups (phenyl and phenoxy) in the 4:6 and the 4:7 positions act as a shield in electron exchange when the complex is oxidized.

Proposed additional applications

The colorimetric potential determination should apply to such redox indicators as N-phenanthranilic acid, diphenylamine and its related derivatives. These redox indicators are not pH dependent.

For non-reversible dye indicators such as amaranth or others for use in iodate oxidations (improved to avoid the use of chloroform as extraction solvent for iodine or iodine monochloride) the method should serve for comparisons of indicator transition potentials.

All the 1:10-phenanthrolines, with but few exceptions, were synthesized in unequivocal processes by Professor Francis Case of Temple University in Philadelphia in co-operation with his associates.[4] Their syntheses have been described in current literature sources. This work on their analytical applications would otherwise not be possible.

Zusammenfassung—Die Bereitung "redox-beschwerter" Bezugslösungen wird beschrieben. Die Redoxpotentiale erstrecken sich stufenweise über einen Bereich von 0.9 bis 1.23 V. Das System Vanadate-Vanadyl wird verwendet. Das Potential hängt im Bereiche 0.1- 6.0 formal vom Anstieg der Schwefelsäurekonzentration ab. Diese Lösungen sind vom Typ Potentialpuffer. Ihr Gebrauch bei der Bestimmung von Redoxpotentialen einer Reihe von Ferrokomplexen substituierter 1,10-phenanthroline wird beschrieben. Die Genauigkeit ist etwa 3 Prozent (oder sogar weniger) geringer im Vergleich mit der auf potentiometrischer Titration basierenden Standardmethode. Die Bestimmung der Potentiale benötigt aussergewöhnlich kurze Zeit.

Résumé—Les auteurs décrivent la préparation de solutions de référence tamponnées en potentiel. Les valeurs des potentiels d'oxydation fournis augmentent graduellement dans le domaine de 0,9 à 1,23 volt. On emploie le système vanadate-vanadyl. La valeur du potentiel augmente avec la concentration de l'acide sulfurique dans le domaine 0,1 à 6 N. Ces solutions sont du type tamponnées en potentiel. On décrit leur utilisation dans la détermination des potentiels d'oxydo-réduction d'une série de complexes ferreux avec les 1-1 ortho-phenanthrolines substituées. La précision obtenue est de l'ordre de 3% au moins comparée aux valeurs standard obtenues à partir des procédés de titrage potentiométriques.

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THE SEPARATION AND DETERMINATION OF NICKEL, CHROMIUM, COBALT, IRON, TITANIUM, TUNGSTEN, MOLYBDENUM, NIOBIUM AND TANTALUM IN A HIGH TEMPERATURE ALLOY BY ANION-EXCHANGE

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Summary—An anion-exchange method of separating the constituents in high temperature alloys has been devised. Nine elements including titanium, tungsten, molybdenum, niobium and tantalum are determined in an alloy on a single sample weight. Any combination of the elements mentioned above may be determined in steels and high temperature alloys with a simple ion-exchange scheme suitable for routine analysis.

THE separation of mixtures of titanium, tungsten, molybdenum, niobium and tantalum by classical methods is one of the most difficult problems in metallurgical analysis. It is not unusual to have these elements as alloying constituents in high temperature alloys. In addition, high temperature alloys usually contain cobalt, nickel, chromium and iron in varying proportions. The classical methods for the separation of titanium, tungsten, molybdenum, niobium and tantalum consist of numerous precipitations which are strongly influenced by the presence or absence of the other elements. Some of the precipitations must be repeated several times in order to obtain satisfactory results. Attempts to analyze these alloys by instrumental means have not been particularly successful. As a result the chemical analysis of the alloying constituents of these materials requires time-consuming work by an experienced analyst.

After a few rather frustrating experiences with alloys of this type, it became apparent that a simplified procedure was desirable in which the presence or absence of a particular element would not alter the procedure appreciably.

Since the author had already made successful applications of ion-exchange resins to other problems in metallurgical analysis,[2,4] a similar approach was selected for the analysis of high temperature alloys. It has already been demonstrated that the separation of some of the refractory elements is possible in mixed HCl–HF medium on strongly basic anion-exchange resins.[1]

Preliminary experiments were based on the precipitation of the refractory metal oxides as a group followed by the ion-exchange separation of the individual elements. This approach was not particularly successful. The difficulty in the method appeared to be in the incomplete precipitation of the oxides. In addition the dissolution of the oxides by a pyrosulphate fusion introduced an amount of salts which caused difficulty in the ion-exchange separations. In view of these difficulties it became apparent that the ideal solution to the problem would be to introduce the entire sample into the ion-exchange column. Several mixtures of HCl–HF were used with some success. However, the most successful medium was found to be a dilute HF solution. If the dilute HF solution of the sample is passed through an anion-exchange resin and eluted with 2.5% HF, the sample constituents are divided into two distinct groups and may be treated separately. The column retains titanium, tungsten, molybdenum, niobium and tantalum and the eluate contains nickel, manganese, aluminium, chromium, cobalt and iron. Subsequent experiments were based on this preliminary separation of the sample into two groups. The refractory elements were separated by successive elutions with various acid solutions and the elements in the 2.5% HF eluate were subjected to a second column separation after evaporation to dryness with hydrochloric acid.

EXPERIMENTAL

Column preparation

The ion-exchange column consisted of 16-inch lengths of one-inch ID polystyrene tubing with a one-quarter inch wall. The lower end of the column was closed off with a section of Lucite rod with three-sixteenths inch hole drilled through its axis. A section one inch long on the end of the Lucite rod is machined down to a three-eighths inch diameter so as to permit the connection of a short length of polyethylene tubing to the column. The other end of the Lucite rod, which is glued to the bottom of the column, is machined so as to have a 45° taper from the one-inch ID of the column to the three-sixteenths inch diameter hole through the rod. This taper eliminates the hold up of the eluted species in the "corner" at the bottom of the column. A short length of quarter inch polystyrene tubing is inserted into the wall of the column about two inches from the top. This piece of tubing allows the connection of the column to an overhead gravity feed by means of polyethylene tubing. The top of the column is sealed with a rubber stopper when the overhead gravity feed is in use. The top of the column should also be threaded and capped with a threaded Lucite cap. This prevents the inadvertent removal of the rubber stopper during the elution. The resin bed is supported by means of a layer of Teflon shavings.

The column is filled with 80 grams of a strongly basic anion-exchange resin, 200–400 mesh, chloride form, after the fine particles are removed from the resin by means of several decantations with water. This quantity of resin will give a column bed 8 in. long which is adequate for the separations in the procedure given below. A $\frac{7}{8}$ in. polyethylene sphere inserted in the column serves to maintain a level surface in the resin bed. Without the sphere the introduction of the sample solution and the eluents to the column disturbs the surface of the resin in such a manner as to cause the sample constituents to be eluted in diagonal instead of horizontal bands. The polyethylene sphere breaks the fall of the solutions sufficiently so as to keep the surface level and give horizontal bands during the elution. Polyethylene is an ideal material for this purpose since it rests on the resin bed when the column is empty, serves as a shield when the solutions are being added to the column, and floats to the surface during the elution so as to give the eluents free access to the entire cross section of the column. In addition polyethylene is not wet by the solution and as a result the last quantities of the sample solution are easily rinsed on to the resin bed. The freshly prepared ion-exchange column should be washed several times alternately with 50-ml portions of 9*M* HCl and 0.5*M* HCl followed by 100 ml of 2.5% HF. A column which has been in use previously may be prepared for separations merely by washing with 50 ml of 2.5% HF.

Procedure

Column separations. Dissolve a l-gram sample in an appropriate mixture of hydrofluoric, hydrochloric and nitric acids and evaporate to dryness on the steam bath. Take up the sample residue in 5 ml of concentrated HF plus 25 ml of water. Warm on the steam bath for about 10 min. and then add an additional 75 ml of water. Transfer the sample solution to the anion-exchange column with 2.5% HF and after the sample solution is rinsed on to the resin bed, elute with 250 ml of 2.5% HF. This eluate will contain elements such as iron, cobalt, nickel, chromium, manganese, aluminium and copper. Further treatment of this eluate will be discussed below.

The column retains elements such as titanium, tungsten, molybdenum, niobium and tantalum. Elute the titanium with 250 ml of 8*M* HCl. Elute the tungsten with 300 ml of a solution which is 10% HF–60% HCl. Elute the molydbenum with 300 ml of a solution which is 20% HF–25% HCl. Elute the niobium with 300 ml of a solution which is 14% NH_4Cl–4% HF. Elute the tantalum with 300 ml of a solution which is 14% NH_4Cl–4% NH_4F.

The material which was used for this particular project contained nickel, chromium, cobalt and iron in the 2.5% HF eluate. Add ten ml of conc. HCl to this fraction and evaporate to dryness on the steam bath. Take up the residue with 9*M* HCl and transfer the solution to a strongly basic anion-exchange column with 9*M* HCl. Elute the nickel and chromium together with 9*M* HCl. Elute the cobalt with 4*M* HCl and finally elute the iron with 0.5*M* HCl.

Treatment of the eluates

Titanium. Add 6 ml of 1 : 1 sulphuric acid to the titanium fraction and evaporate to fumes of sulphuric acid. Cool to room temperature, add several grams of ice from distilled water and 0.5 ml of 30 vol. per cent hydrogen peroxide and dilute to 100 ml in the volumetric flask. Transfer an appropriate aliquot to a 250-ml beaker, add 150 ml of water and a measured excess of EDTA. Add 10 ml of a sodium acetate-acetic acid buffer and if necessary adjust the pH to approximately 4.8 with a concentrated sodium hydroxide solution. Add two to three drops of a metalfluorechromic indicator and back-titrate the excess of EDTA with a standard copper solution using ultraviolet light as the sole source of illumination.

Tungsten. To the tungsten fraction add 6 ml of 1 : 1 sulphuric acid and evaporate the solution to fumes of sulphuric in order to remove the fluoride. Cool to room temperature and add several grams of ice followed by 25 ml of water, and 1 : 1 ammonium hydroxide until the tungstic acid precipitate just redissolves. Add 20 ml of the sodium acetate–acetic acid buffer and if necessary adjust the pH to approximately 4.8 with dilute acid. Add a small excess of 8-hydroxyquinoline in dilute acetic acid. Bring the solution to the boil on the hot plate and then digest for about 5 minutes at about 80° to 90°. Cool the solution to room temperature and filter the tungsten 8-hydroxyquinolate on a weighed Gooch crucible. Wash the precipitate several times with water, dry at 110° for 1 hour and weigh the crucible plus precipitate. The factor for tungsten is 0.365.

Molybdenum. Treat the fraction containing the molybdenum in an identical manner as that described above for tungsten. The factor for molybdenum is 0.2305.

Niobium. Add 9 g of boric acid to the niobium fraction. After the boric acid is dissolved, transfer the solution to a glass beaker, add 60 ml of 1 : 1 sulphuric acid and cool to 10° in ice. Add a slight excess of cupferron and filter the niobium cupferrate. Wash the precipitate thoroughly with a 5% sulphuric acid solution which is saturated with cupferron in order to remove the ammonium salts from the precipitate. Cautiously ignite the niobium cupferrate to the oxide and weigh as Nb_2O_5.

Tantalum. Treat the tantalum fraction in the same manner as is described above for niobium.

Nickel and chromium. Evaporate the nickel and chromium fraction to dryness to remove the excess of hydrochloric acid. Dissolve the residue with water plus a small amount of dilute HCl and tranfser to a 100-ml volumetric flask. Transfer an appropriate aliquot to a 250-ml beaker. Add 150 ml of water, 10 ml of sodium acetate-acetic acid buffer and a measured excess of EDTA over that which would be necessary for the nickel which is present in the sample. Add 2 to 3 drops of a metal-fluorechromic indicator and back-titrate the excess of EDTA with a standard copper solution. This titration should be carried out at room temperature in order to avoid interference from the chromium present in this aliquot. Calculate the per cent nickel in the sample from the excess of EDTA and the copper used in the back-titration. To the solution in which the nickel was just determined add a measured excess of EDTA over that which would be required for the chromium present in the solution. Place the beaker on a hot plate and boil the solution for 15 minutes in order to form the chromium-EDTA complex. Back-titrate the excess of EDTA with the standard copper solution using ultraviolet light. Calculate the per cent chromium from the amount of EDTA added and the copper used in the back-titration.

Cobalt fraction. Transfer the cobalt fraction to a 100-ml volumetric flask and take an appropriate aliquot in a 250-ml beaker. Add 150 ml of water, a measured excess of EDTA, and 10 ml of ammonium chloride ammonium hydroxide buffer (pH approximately 9.5). If necessary adjust the pH to approximately 9.5 with ammonium hydroxide, add 2 to 3 drops of a metalfluorechromic indicator, and back-titrate the excess of EDTA with a standard copper solution. Calculate the per cent cobalt from the amount of EDTA added and the volume of standard copper solution used for the back-titration.

Iron fraction. Transfer a suitable aliquot of the iron fraction to a 250-ml beaker. Add a measured excess of EDTA, dilute to approximately 150 ml, and adjust the pH to approximately 4.8. Add 2 to

3 drops of a metalfluorechromic indicator and back-titrate the excess of EDTA with a standard copper solution to the quenching of the fluorescence of the free indicator.

DISCUSSION

The volumes of eluents used during the elutions from the polystyrene column are suitable for the column dimensions and the resin particle size given under *Column Preparation.* If a smaller amount of eluent is used there is a possibility of obtaining incomplete separations of the refractory metals. The use of larger volumes of eluent does not alter subsequent separations. The elution scheme shown in Fig. 1 is quite versatile and may be used for many combinations of refractory elements. In the event that some of the elements are absent in a sample one merely skips the elution step for those elements and proceeds with the elution of the next element on the flow sheet. If one or more elements are missing the volumes of eluents for the elements present are unchanged. In addition any eluent on the flow sheet will elute (in 300 ml) all the elements that precede the eluent on the flow sheet. For example, the 20% HF–25% HCl eluent elutes titanium and tungsten as well as molybdenum. This is advantageous on occasions where one desires to determine one or two of the elements at the end of the flow sheet and does not need to conduct all the elutions preceding it. The procedure may be applied to the determination of one or all of the above mentioned elements in stainless steels as well as in high temperature alloys.

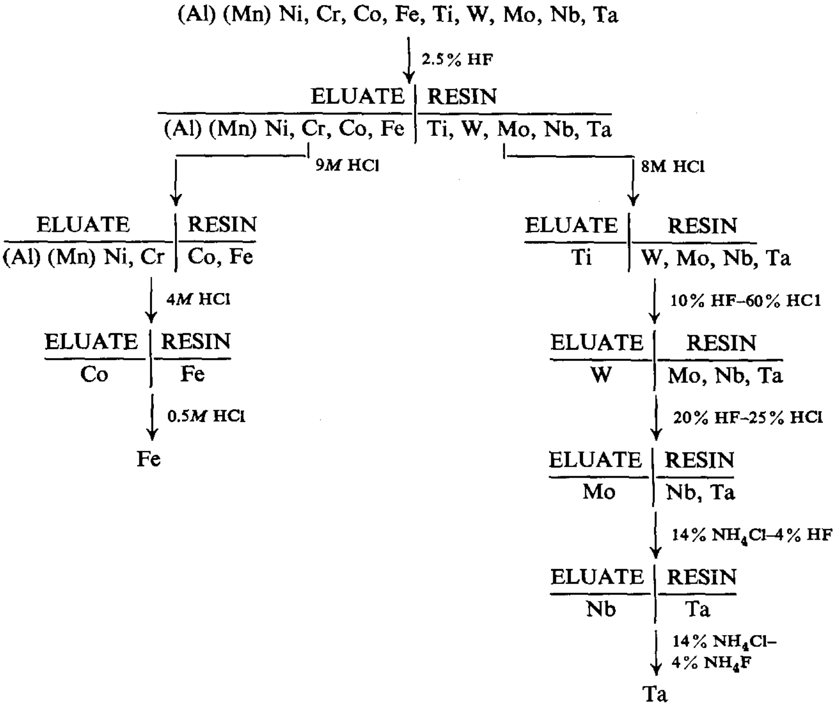

FIG. 1.—Flow sheet for the analysis of a high temperature alloy

The 2.5% HF fraction which is first converted to a chloride solution is usually separated in small glass columns. For example with the alloy shown in Table I the glass columns contained 10 gms of Dowex 1 × 8, 200–400 mesh, chloride form, in a resin bed 1 cm ID × 12 cm long. The use of a smaller column permits more rapid separations with smaller volumes of eluents.

Additional elements may be accommodated in this portion of the procedure. For example aluminium and manganese will be found in the 9*M* HCl eluent along with nickel and chromium. With all four elements the most suitable procedure is to take an aliquot for an aluminium, manganese and nickel determination and remove the chromium by volatilization of chromyl chloride from a perchloric acid solution. The diluted solution is then passed through a cation-exchange resin. Aluminium may then be eluted with a dilute HF solution and then nickel and manganese with 4*M* HCl. Chromium is determined in a separate aliquot.

TABLE I.—COMPOSITE SAMPLE TO SIMULATE A HIGH TEMPERATURE ALLOY

Ni found, *mg*	Cr found, *mg*	Co found, *mg*	Fe found, *mg*	Ti found, *mg*	W found, *mg*	Mo found, *mg*	Nb found, *mg*	Ta found, *mg*
19.2	17.6	43.0	22.0	70.6	45.9	38.5		
19.2	17.6	43.0	22.0	70.6	45.9	38.5	31.6	22.3
19.2	17.6	43.0	22.0	70.1	46.1	39.1	31.5	22.3
19.3	17.6	43.0	22.1	70.7	46.6	39.4	32.6	22.6
19.1	17.7	43.0	22.0	69.7	46.3	39.6	32.8	22.4
19.2	17.7	43.0	21.9	69.4	46.4	39.4	33.4	22.7

Nominal values—Ni, 19.2 mg; Cr, 17.5 mg; Co, 42.9; Fe, 22.0 mg; Ti, 70.5 mg; W, 46.2 mg; Mo, 39.8 mg; Nb, 32.1 mg; Ta, 22.0 mg.

If copper is present in the original sample it will be found in the 2.5% HF eluate. In this case the separation of the elements in the 2.5% eluate must be done on a larger column in order to separate copper from cobalt.[2]

Calcein W (0.1% in water) was used as a metalfluorechromic indicator for all the chelometric titrations in order to avoid any interference in the detection of the end-point by highly coloured EDTA complexes.[5,6] An apparatus for these titrations has been previously described.[3]

Zusammenfassung—Eine Anionenaustauscher-Methode zur Trennung der Bestandteile in Hochtemperaturlegierungen wird beschrieben. Neun Elemente, darunter Titan, Wolfram, Molybdän, Niob und Tantal werden in einer Einwaage bestimmt. Jede beliebige Kombination der oben erwähnten Elemente in Stählen und Hochtemperaturlegierungen kann mittels der einfachen Methode rutinemässig bestimmt werden.

Résumé—L'auteur a imaginé une méthode par échange anionique pour séparer les constituants des alliages réfractaires. On a dosé neuf éléments, dont le titane, le tungstène, le molybdène, le niobium et le tantale, dans un alliage sur une seule prise d'essai.

On peut doser, dans des aciers et des alliages réfractaires toute combinaison des éléments mentionnés ci-dessus par un procédé simple d'échange d'ions adapté à l'analyse de routine.

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THE REDOX PROPERTIES OF SOME ALKOXYL-SUBSTITUTED BENZIDINES

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Summary—An account is given of the redox properties of 3-methoxy-, 3-ethoxy-, 3:3′-dimethoxy- and 3:3′-diethoxybenzidine. These compounds are oxidised to cherry-red or orange-red colours. Their sensitivities towards oxidants and their transitional potentials have been determined and their behaviour as indicators in redox titrations has been examined.

INTRODUCTION

Weeks[1] first proposed *o*-dianisidine (3:3′-dimethoxybenzidine) as a redox indicator in dichromate titrations, but it has not come into general use for this purpose. Although it has been extensively used as an indicator in the titration of zinc with ferrocyanide,[2,3] a new range of naphthidine indicators proposed by Belcher, Nutten and Stephen[4–6] have end-point colour changes considerably better than those of *o*-dianisidine. Better end-points have also been obtained when 3-methyl- and 3:3′-diethylbenzidine are used as indicators in the microdetermination of gold with quinol[7] in place of *o*-dianisidine which was normally used for this determination.[8,9] Although these new indicators have tended to replace *o*-dianisidine in most titrations, the redox properties of the latter have even recently been applied in analytical chemistry; the determination of chromate,[10] ferricyanide,[11] and blood and urine glucose[12] are examples. In addition, like other benzidine compounds, it has the property of forming complexes and salts with metals and acids respectively and it has been recommended as a reagent for copper and thiocyanate,[13] and for molybdenum,[14] tungsten[15] and vanadate.[16]

In view of the considerable interest in *o*-dianisidine as an analytical reagent an investigation of other benzidine derivatives containing alkoxyl groups has been made. 3-Methoxy-, 3-ethoxy- and 3:3′-diethoxybenzidine have been prepared and their redox properties examined spectrophotometrically and potentiometrically (together with *o*-dianisidine) in order to assess their applicability as analytical reagents.

EXPERIMENTAL

Indicator solutions: 0·5% in glacial acetic acid.

Sensitivity determinations

(*i*) *Neutral solution:* 2 ml of the neutral test solution and 1 drop of the indicator solution were added to a micro-test tube. The contents of the tube were shaken and the colour formed was viewed against a white background. The procedure was repeated with more dilute solutions of the oxidising ions until a yellow or light brown colour was just detectable after 2 minutes of mixing.

(*ii*) *Acid solution:* The above procedure was repeated but with 1 ml of the test solution, 1 ml of 0·2*N* hydrochloric acid and 1 drop of the indicator solution.

When ferricyanide was used as the neutral ion test solution, 1 drop of 0·01*M* zinc sulphate solution was added before adding the indicator solution.

The results obtained for benzidine and the four alkoxyl derivatives are given in Table I.

TABLE I.—SENSITIVITIES TOWARDS OXIDANTS

Identification limit (μg) in 2 ml of solution

(i) Neutral solution

Reagent	Oxidant										
	$Cr_2O_7^{2-}$	VO_3^-	IO_4^-	MnO_4^-	Fe^{3+}	$S_2O_8^{2-}$	IO_3^-	BrO_3^-	Ce^{4+}	OCl^-	$Fe(CN)_6^{3-}$
Benzidine	100	40	80	0·2	16	4	>2000	>2000	1	0·6	1·0
3-MeO-benzidine	10	20	20	0·4	11	6	2000	>2000	1	0·7	0·6
3-EtO-benzidine	10	30	40	0·4	16	3	>2000	>2000	3	1·9	0·6
3:3′-diMeO-benzidine	4	13	10	0·2	10	2	400	>2000	1	0·6	0·4
3:3′-diEtO-benzidine	4	10	10	0·3	11	3	1000	>2000	1	0·6	0·6
(ii) Acid solution											
Benzidine	5	50	200	0·2	25	20	20	250	1·0	0·7	13
3-MeO-benzidine	2	20	40	0·2	13	50	10	500	1·3	0·7	10
3-EtO-benzidine	2	20	100	0·3	20	33	8	500	1·3	0·7	5
3:3′-diMeO-benzidine	1	13	40	0·2	10	20	7	200	1·0	0·4	4
3:3′-diEtO-benzidine	1	20	40	0·2	20	33	7	250	1·3	0·4	2

Spectrophotometric studies

Five drops of the indicator solution were mixed with 100 ml of 0·5M–5M sulphuric acid, followed by 1 drop of 0·1N ceric sulphate solution. The colours formed were too unstable for the absorption spectra of the red oxidation products to be plotted and only λ_{max} values could be recorded. A Unicam S.P. 600 spectrophotometer was used.

TABLE II.—TRANSITION POTENTIALS AT 18°–20°, REFERRED TO THE STANDARD HYDROGEN ELECTRODE

Indicator	Acid concentration, M H_2SO_4				
	0·1	0·5	1·0	2·0	4·0
3-MeO-benzidine	0·79	0·83 (0·81)	0·82 (0·80)	0·83 (0·83)	0·84 (0·85)
3-EtO-benzidine	0·78	0·82 (0·80)	0·80 (0·80)	0·82 (0·81)	0·83 (0·85)
3:3′-diMeO-benzidine	0·75	0·79 (0·77)	0·78 (0·76)	0·80 (0·79)	0·81 (0·82)
3:3′-diEtO-benzidine	0·76	0·79 (0·78)	0·79 (0·75)	0·81 (0·80)	0·81 (0·83)
Diphenylamine-sulphonic acid	0·81	0·82 (0·81)	0·83 (0·85)	0·80 (0·82)	0·75 (0·76)
Ferroïn		(1·08)	(1·10)	(1·07)	(1·00)

Values not in parentheses are those for the Fe^{2+}–Fe^{3+} and the $Cr_2O_7^{2-}$–Cr^{3+} systems, whilst those in parentheses are for the Fe^{2+}–Fe^{3+} and the Ce^{4+}–Ce^{3+} systems.

Transition potentials

The apparatus, reagents and procedure are described by Belcher, Nutten and Stephen.[17] A 0·1N solution of ferrous ammonium sulphate of known acid content was titrated potentiometrically against a 0·01N solution of the oxidant of the same acid content, in the presence of 5 drops of the indicator solution. Just before the theoretical end-point, the 0·1N solution of the oxidant was replaced by a 0·01N solution which was added dropwise. The transition potential was obtained when the first trace of a red coloration appeared. The results obtained when using dichromate and cerium^{IV} as oxidants are given in Table II.

Application as redox indicators

The solutions and titration procedures have been described previously.[6] Ten drops of the indicator solutions were required for the titrations of dichromate and cerium^{IV} with iron^{II} solution.

Preparation of amines

The preparations of 3-methoxy-,[18] 3-ethoxy-[19] and 3:3′-diethoxybenzidine[20] are described in the literature. *o*-Dianisidine is available commercially.

RESULTS AND DISCUSSION

Colour reactions and sensitivity tests

The two disubstituted derivatives give a bright cherry-red colour on being oxidised in acid solutions whereas the monosubstituted derivatives give a more orange coloured oxidation product. This visual observation is confirmed by the λ_{max} values, those of the oxidised monosubstituted derivatives being 435 mμ to 440 mμ in 0·5*M* to 4*M* sulphuric acid solutions and those of the oxidised disubstituted derivatives being 450 mμ except in the case of 3:3′-diethoxybenzidine in 4*M* sulphuric acid solution, where the value is 455 mμ.

The stability of the colours increase with increasing acidity, but even in 4*M* sulphuric acid solution the colours are too unstable for an accurate plot of the absorption spectra to be made. The colours formed at these high acidities are less intense, however, than those formed at lower acidities. The disubstituted derivatives oxidise to more stable colours than the monosubstituted derivatives.

The reduction of the red colours back to the colourless free amines is very sluggish. This is the reason for the appearance of a red coloration before the true end-point has been reached and is the chief cause for the replacement of *o*-dianisidine with more reversible redox indicators in most titrations.

In the sensitivity tests it is interesting to note that only in the case of ferricyanide ion in acid solution is 3:3′-diethoxybenzidine much more sensitive than the other three compounds. The sensitivities of the amines to $Cr_2O_7^{2-}$, IO_3^- and BrO_3^- is greater in acid solution than in neutral solution, whilst it is the reverse in the case of IO_4^-, $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$, and approximately of the same order in the case of VO_3^-, MnO_4^- and Ce^{IV}. In general, the order of the sensitivities in both acid and neutral solutions is 3:3′-dimethoxy- = 3:3′-diethoxy- > 3-methoxy- > 3-ethoxybenzidine > benzidine.

Transition potentials

Although Crawford and Bishop[3] determined the oxidation potential of *o*-dianisidine by direct titration with ceric sulphate, it has been pointed out[17] that this value is of little practical importance. The potentials recorded in Table II are the potentials at which the amines, used as indicators, first show a change of colour in actual redox titrations. In most cases the transition potentials found when using cerium^{IV} as oxidant are slightly less than those found when using dichromate. This observation which is probably associated with the so-called inductive effect of iron^{II} in the dichromate-chromous system has also been made in the naphthidine series.[21] At all the acid concentrations examined, the two monosubstituted derivatives have higher transition potentials than the disubstituted derivatives with 3-methoxy- and 3:3′-dimethoxybenzidine having the highest and lowest values respectively.

Application as redox indicators

As a result of the appearance of a slight red coloration before the end-point and the slow development of the bright cherry-red colour from an initially orange colour, none of the alkoxybenzidines is wholly satisfactory as a redox indicator. The former disadvantage is overcome to some extent if the indicator is added just before the end-point. Under these conditions the indicator blank is equivalent to 0·04 ml of

0·1*N* oxidant. In the titration of iron^{II} with dichromate, the presence of phosphoric acid, which is necessary when using diphenylaminesulphonic acid, causes overtitration and a retardation of the development of the full red colours. In general, the monosubstituted derivatives give better end-points in the various concentrations of sulphuric acid solutions. These indicators are more suitable than diphenylaminesulphonic acid at higher acidities (4*M* sulphuric acid), as the marked drop in the transition potential of the latter indicator gives rise to undertitrations. In fact the transition potentials of the alkoxybenzidines increase to values greater than those of diphenylaminesulphonic acid at these high acid concentrations.

Much better end-points are obtained in the titration of iron^{II} with ceric sulphate, especially with 3:3′-diethoxybenzidine. Stoicheiometric results are obtained in 0·5–4·0*M* solutions of sulphuric acid. None of the indicators can be recommended in place of ferroïn, although it should be noted that this latter indicator does not give a satisfactory colour change at concentrations above 4*M* with respect to sulphuric acid; the alkoxybenzidines behave normally under these conditions.

o-Dianisidine has been extensively used in the titration of zinc with ferrocyanide, but the present comparison shows that, whereas the two monosubstituted derivatives give only slightly inferior end-points to that of *o*-dianisidine, 3:3′-diethoxybenzidine gives a much sharper end-point. In the titration of cadmium with ferrocyanide, all four alkoxybenzidines give end-points which are difficult to detect. This observation has already been made in the case of *o*-dianisidine.[22]

CONCLUSION

Although the four alkoxybenzidines studied cannot be recommended for most titrations where there are already suitable redox indicators available, they may be of some importance (especially 3:3′-diethoxybenzidine which gives sharper end-points) in titrations of dichromate and cerium^{IV} with iron^{II} at higher acidities ($>4M$ sulphuric acid) where the redox indicators normally used do not function satisfactorily.

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Zusammenfassung—Das Redox-Verhalten folgender Substanzen wird studiert: 3-Methoxy-, 3-Äthoxy-, 3,3′-Dimethoxy- und 3,3′-Diäthoxybenzidin. Die Substanzen werden leicht zu kirschroten oder orangeroten Verbindungen oxydiert. Die Empfindlichkeit gegenüber oxydierenden Substanzen und das Oxydationspotential wurde bestimmt. Über die Anwendung der Verbindungen als Redoxindicatoren wird berichtet.

Résumé—Les auteurs donnent une interprétation des propriétés oxydoréductrices de dérivés de la benzidine (méthoxy-3, ethoxy-3, dimethoxy-3.3′ et diethoxy-3.3′ benzidine). Ces composés sont oxydés en substances rouge cerise ou rouge orangé. Leur sensibilité à l'égard des oxydants et leur potentiel de transformation ont été déterminés et leur comportement comme indicateur dans les titrages d'oxydo-réduction a été étudié.

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AN EDTA-POLAROGRAPHIC METHOD FOR THE DETERMINATION OF TELLURIUM IN LEAD ALLOYS*

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Summary—A procedure is described for the polarographic determination of tellurium in lead alloys, without resorting to prior separative techniques. Interference by Cu, Cd, Tl, As, and Sb is discussed.

EXISTING polarographic,[1] spectrophotometric,[2–5] and other,[6–7] procedures for the determination of tellurium have not proved wholly satisfactory in the presence of large amounts of lead, as, for example, in alloys with this element. Here prior separative procedures involving precipitation[1,2,15] or extraction[16] have proved difficult, if not impossible,[17] in conjunction with polarography. The half wave potentials of Te^{IV} and Pb^{II} are almost identical and a survey of the literature reveals that no polarographic technique applicable to this determination has been developed.

However, it is known,[12,13] that in the presence of EDTA the half wave potential of the lead ion is shifted with increase in pH of the solution towards more negative values. Lead occurs usually as a complex cation and tellurium as the tellurite anion. In Group VIa of the Periodic Classification, metallic character, as well as tendency towards formation of complex ions, increases with increasing atomic number. Tellurium, however, differs considerably from such a metallic element as lead in its behaviour towards EDTA, being complexed more strongly than selenium, although much less strongly than polonium. On the basis of these facts, this paper describes a procedure for the polarographic determination of tellurium in the presence of lead.

EXPERIMENTAL

A standard aqueous solution of tellurium was prepared from TeO_2, or alternatively by dissolving metallic tellurium in nitric acid. Polarographs LP55 (Czechoslovakia) and PO3 (Radiometer, Copenhagen) were employed, deaeration of solutions being accomplished with propane gas.[11]

PRELIMINARY INVESTIGATIONS

The polarographic characteristics of tellurium may be recommended for analytical purposes. In the most common state, +4, a well defined wave is obtained in NH_3—NH_4Cl solution,[8,9] at −0·7 V (S.C.E.), involving reduction to metallic Te(O). Within limits, wave height is here linearly proportional to concentration. At −1·1 V further reduction to the −2 state takes place, an exceptionally high maximum being observed, and reaction between Te (+4) and Te(−2) occurring in the vicinity of the mercury drop.[9,10] This potential should be avoided in analytical work, owing to the large amount of free tellurium formed, with the consequent possibility of damage to the capillary orifice. Even at the lower potential free tellurium is liberated, but its adherence to the mercury drop protects the capillary tip from such damage. The observed disturbances in the solution at −1·1 V (appearance of Te suspension during maximum) were recorded cinematographically; further observations and conclusions concerning the lowering of current after the maximum will be published later.

In the presence of EDTA, in solution of pH 10, the lead half-wave potential is shifted to −1·1 V.

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Under these conditions, however, the tellurium wave at −0·7 V cannot be utilised for measurement, since the high instrumental sensitivity necessary for the determination of tellurium in small amounts reveals the beginning of an increase in current at −0·6 V, due to the high concentration of lead present. Furthermore, the definition of the tellurium wave is seriously affected in solutions of high pH, although the influence of EDTA is negligible.

A satisfactory compromise with these conflicting pH requirements was found in EDTA—NH_4Cl—NH_4NO_3 solution, adjusted using ammonium hydroxide to pH 8–9. The concentrations of these reagents are not critical, but best results were obtained using the following procedure.

Detailed procedure

1. Dissolve 0·5 g of Pb/Te alloy in 6 ml of nitric acid (1 : 1), add 10 ml of 10% EDTA solution and adjust to approximately pH 7 using ammonium hydroxide. Add 0·5 g of ammonium chloride, followed by 1 ml of 15% ammonia solution, and make up to 25 ml.
2. Remove oxygen from solution by means of a stream of propane, nitrogen or argon gas.
3. The half-wave potential of the Te^{IV}–Te^0 wave is −0·45 V with respect to internal mercury pool. Record the polarogram from −0·2 V onwards, increasing the voltage very gradually (100 mV/cm).
4. Calculate the amount of tellurium present from the prepared calibration curve.

RESULTS

Fig. 1 shows a typical polarogram obtained by this procedure. The minimum amount of tellurium which can be determined is 0·01% of the lead concentration, the calibration graph being strictly linear in the range 0·01–0·20%. The precision of the determination was investigated statistically,[14] the value of 2·4% error being obtained for samples containing 0·1% tellurium.

Interferences of some cations were investigated. Both the copper and cadmium waves are shifted to more negative potentials in the presence of EDTA, sufficiently far from that of tellurium to preclude their interference. Arsenic, antimony and thallium interfere when present in concentration greater than 0·01%, but in the case of the last-named the tellurium wave height may be corrected for the amount of thallium present.

The results are very satisfactory and the method appears superior to existing gravimetric and colorimetric procedures. The time required is relatively short and no special technique is demanded of the operator.

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Zusammenfassung—Eine Methode zur polarographischen Bestimmung von Tellur in Bleilegierungen ohne vorhergehende Trennungen wurde entwickelt. Störungen durch Cu, Cd, Tl, As und Sb sind besprochen.

Résumé—Les auteurs décrivent une méthode de dosage polarographique du tellure dans des alliages de plomb, sans recourir à des techniques de séparation préalables. On discute l'interférence du Cu, Cd, Tl, As et Sb.

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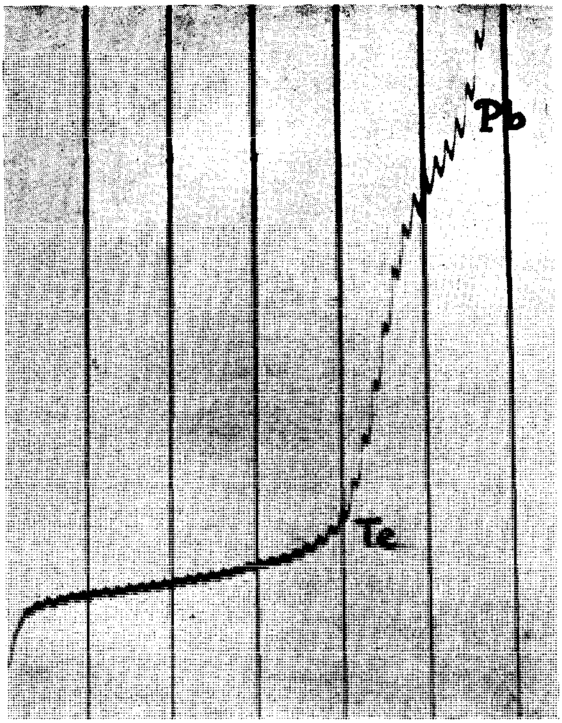

FIG. 1.—Polarogram of tellurium in the presence of lead, using the procedure described. 0·1 % Te alloy. Polarograph LP55, simple vessel with mercury pool anode, 100 mV per abscissa, sensitivity 1/10.

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TITRATION OF OXALIC ACID WITH CERIUM^{IV} SULPHATE AT ROOM TEMPERATURE USING FERROÏN AS INTERNAL INDICATOR

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Summary—Evidence is presented to show that, contrary to the statements of earlier workers, the reaction between ceric sulphate and oxalic acid is quite rapid in hydrochloric acid medium specially in the presence of iodine monochloride as catalyst. We have now found that the need for a temperature of 50° in the cerimetric titration of oxalic acid using ferroïn as indicator is not due to the sluggishness of the reaction between oxalic acid and Ce^{IV} (as believed by Willard and Young) but because of the slow reaction between oxidised ferroïn and oxalic acid in the presence of sulphate ion derived from ceric sulphate. Conditions have now been developed for the titration of oxalic acid with ceric sulphate at room temperature in 1*N* hydrochloric acid medium using ferroïn as indicator, and barium ion as scavenger for sulphate ion, which latter markedly retards the reaction between oxalic acid and oxidised ferroïn, as well as that between oxalic acid and Ce^{IV}. The method now developed has several advantages over that prescribed by Willard and Young because it avoids the high temperature of 50°, where the ferroïn indicator is found to undergo some dissociation. It also avoids the use of the iodine monochloride catalyst.

BENRATH and Ruland[1] studied the kinetics of the reaction between cerium^{IV} sulphate and oxalic acid and showed that at room temperature the reaction is very slow in dilute solutions, especially towards the completion of the reaction. Furman[2] appears to be the first to make a study of this reaction for the purpose of titrimetric analysis. He obtained satisfactory results when the titration of ceric sulphate with an oxalate was carried out in sulphuric acid medium at 50°–60°, the end-point being detected electrometrically. Using the disappearance of the yellow colour of the ceric ion as end-point with decinormal solutions gave a value 0·03 ml earlier than the potentiometric end-point. Furman stated that the reverse titration, namely, the titration of oxalate with ceric sulphate is not practicable in sulphuric acid medium because of the slow rate of reaction. Willard and Young[3] investigated in detail the titration of oxalate with ceric sulphate over a wide range of concentration and temperature. They observed that below 70° the potential equilibrium at the end-point was attained too slowly. The equilibrium was established rapidly if the titration was carried out "near boiling point" in hydrochloric acid solution. The titration could be carried out in the presence of as much as 60 ml of 73% perchloric acid or 50 ml of glacial acetic acid per 200 ml of solution instead of sulphuric or hydrochloric acid and the end-point equilibrium was rapid. The presence of even 5 ml of conc. nitric acid in this same volume, however, gave too high a value for the ceric sulphate, showing that this acid had a slight effect on the oxalate. Phosphoric and hydrofluoric acids must be absent, even if considerable hydrochloric acid was present, as they caused the formation of insoluble cerium salts. They further observed that the electrometric titration of oxalic acid could be satisfactorily carried out at room temperature in a hydrochloric acid medium if iodine chloride was present as a catalyst. Iodide and iodate were also found to act as catalysts but not as effectively as iodine chloride. Willard and Young also stated that the titration of oxalate could be satisfactorily carried out at room temperature in the presence of iodine monochloride, using methylene blue as internal indicator in hydrochloric acid medium. It was recommended that the indicator should be added towards the close of the titration, as it tended to be destroyed if present from the start.

In a subsequent communication, Willard and Young[4] examined the use of ferroïn as internal indicator in the titration of oxalate with ceric sulphate. They stated that the reaction of sodium oxalate with ceric sulphate at room temperature in a hydrochloric acid solution containing iodine chloride as catalyst was not rapid enough for the use of *o*-phenanthroline ferrous complex as indicator; and that "a temperature of 50° seemed most satisfactory, for at higher temperatures, too much of the indicator was destroyed, *while at much lower temperatures this reaction was not sufficiently rapid*". It was possible to titrate rapidly to within five or six drops of the end-point. The solution was then reheated to 50° and the titration completed. The Willard and Young procedure does not yield satisfactory results in the hands of all workers. Vogel[5] has stated that "he could not obtain satisfactory results by the use of the iodine monochloride as catalyst and ferroïn as indicator". He has recommended running the ceric sulphate solution into a hot solution of oxalic acid solution until the solution acquires a permanent faint yellow colour, and applying a blank correction; or alternatively adding an excess of ceric sulphate solution to the oxalic solution warming the mixture to 50° for five minutes, and, after cooling, titrating the excess of ceric sulphate with a standard ferrous ammonium sulphate solution, using N-phenylanthranilic acid or ferroïn as indicator as recommended earlier by Hammet, Walden and Edmonds,[6] Lindner and Kirk[7] and others. Rappaport[8] determined the excess ceric sulphate iodimetrically. Szebellédy and Tanay[9] investigated the use of manganous salts as catalysts. For the microtitration of oxalate in N sulphuric acid at 50° with $0{\cdot}01N$ ceric sulphate using ferroïn as indicator, they employed 2% of manganous sulphate or chloride. Wheatley[10] stated that the titration can be performed in the cold if the manganous salt concentration is increased to 5 per cent. Watson[11] prefers to employ a temperature of 40°–50° in the same titration.

In our opinion, the explanation offered by Willard and Young for the need of a temperature of 50° for the titration of oxalate with ceric sulphate using ferroïn as indicator is not quite satisfactory. If the reaction between ceric sulphate and oxalate is slow (as believed by Willard and Young) at room temperature in hydrochloric acid medium, even in the presence of iodine monochloride as catalyst, one fails to understand how the titration is possible at room temperature with an electrometric end-point or with methylene blue as internal indicator. In this connection, it is pertinent to note that in the electrometric titration Willard and Young observed that the equilibrium potentials were attained rapidly after the addition of each drop of ceric sulphate. The retardation of the reaction by sulphuric acid introduced through the ceric sulphate must be applicable equally to the titrations with the electrometric and colorimetric end-points. We believe that the explanation for the need of a temperature of 50° must be sought in quarters other than the slowness of the reaction between ceric sulphate and oxalic acid.

The present investigation has been undertaken with the purpose of clarifying the position.

EXPERIMENTS AND OBSERVATIONS

We have observed that the reaction between cerium^{IV} sulphate and oxalic acid is rapid at low concentrations of reactants and at all concentrations of hydrochloric acid between 0·2N and 6·0N. This can be seen by the fact that the yellow colour of ceric ion is rapidly discharged when one drop of 0·05N cerium^{IV} sulphate is mixed with one drop of 0·1N oxalic acid in a total volume of 5 ml of hydrochloric acid (0·2N to 6·0N). The reaction is very fast even in the absence of a catalyst like iodine monochloride. If the cerium^{IV} sulphate and oxalic acid are taken at high concentrations (0·05N), the reaction, although quite rapid in the early stages, becomes rather slow towards the end. We have also observed that the reaction is strongly retarded by the sulphate ion. The inhibition can be observed even at 0·5N sulphate ion concentration. The retardation of the cerium^{IV} oxalate reaction by the sulphate ion is counteracted by iodine monochloride. In view of this, the titration of oxalic acid with cerium^{IV} sulphate is possible in hydrochloric acid medium at room temperature, when iodine monochloride is used as a catalyst as already observed by Willard and Young in their electrometric titrations.

For the above titration to be carried out using redox indicators, one has to take into account not merely the speed (1) of the reaction between oxalic acid and ceric sulphate but also of the reactions between (2) the indicator and ceric sulphate and (3) oxidised indicator and oxalate. Reaction (3) has not been apparently taken into account by Willard and Young in their study of this titration with ferroïn as indicator. It is well known that the reaction between ferroïn and cerium^{IV} sulphate is quite fast in either sulphuric or hydrochloric acid medium. In order to ascertain the nature of the reaction between oxidised ferroïn (ferriïn) and oxalic acid, we have now carried out experiments of which the results are summarised in Table I.

From these results it may be concluded (1) that the reduction of oxidised ferroïn by oxalic acid is very rapid in 0·2N to 0·5N hydrochloric acid. But it is retarded as the acid concentration is increased. (2) Sulphate ion retards the reaction very markedly even in 0·2N hydrochloric acid. (3) From Experiments IIIa and IVa, although the reduction of ferriïn is very slow in 1N and 2N hydrochloric acid, the addition of a trace of cerium^{IV} produces the red colour due to ferroïn. Thus it is evident that the slow reaction between ferriïn and oxalic acid is induced by the rapid reaction between cerium^{IV} and oxalic acid. (4) This induction does not occur in 3N hydrochloric acid as evidenced by Experiment Va. (5) The induction noted in Experiments IIIa and IVa does not occur in the presence of sulphate ion as can be seen from Experiments IIIc and IVc. (6) The slow reaction between ferriïn and oxalic acid in 1N to 2N hydrochloric acid is markedly catalysed by iodine monochloride at the room temperature. But this catalysis is not much in evidence in the presence of sulphate ion (*Vide* Experiments IIIe and IVe). (7) The catalysis by iodine monochloride becomes prominent only at 50° in the presence of sulphate ion. From Experiment IIIf, it is evident that a bright red colour results from the reduction of ferriïn by oxalic acid in 30 seconds in 1N hydrochloric acid; if the acid concentration is 2N, the bright red colour appears in 45 secs (Experiment IVf). If the hydrochloric acid concentration is 3N, the reduction of ferriïn takes 60 secs as evidenced by Experiment Vf.

Now, from Experiments IIIf, IVf and Vf, it becomes clear that the reduction of ferriïn by oxalic acid is so greatly retarded by sulphate ion that it can only take place with noticeable speed provided (1) the temperature is 50° and (2) iodine monochloride is present as a catalyst. Even under these conditions, the speed is not fast enough with the result that one has to wait for 30 secs, 45 secs, or 60 secs, according as the hydrochloric acid medium used is, 1N, 2N or 3N. Our experiments also indicate that titration of oxalic acid with cerium^{IV} sulphate should be more satisfactory in 1N than in 2N or 3N hydrochloric acid, which is actually the case. Also the need for a higher temperature and the iodine monochloride catalyst arise more from the retarding effect of the sulphate ion on the reaction between the oxidised ferroïn and oxalic acid, rather than because of any other system involved in the titration. Sulphate ion does not retard the oxidation of ferroïn by ceric sulphate.

From the foregoing, we may also conclude that if the sulphate ion is removed from the system, the titration of oxalic acid with ceric sulphate should be possible even at room temperature using ferroïn as indicator and without the use of the iodine monochloride catalyst. The validity of this conclusion has been tested by titrations of oxalic acid with ceric sulphate, adding sufficient barium chloride to remove the sulphate ion from the system as insoluble barium sulphate as the titration proceeds. In consequence, the following procedure is recommended.

TABLE I.—25 ML OF HYDROCHLORIC ACID + 1 DROP OF OXIDISED FERROÏN (0·01*M*) + 1 DROP OF 0·05*N* OXALIC ACID. THE TIME REQUIRED FOR THE APPEARANCE OF THE RED COLOUR DUE TO THE FORMATION OF FERROÏN FROM THE TIME OF THE ADDITION OF OXALIC ACID IS NOTED.

Experiment No.	Concentration of hydrochloric acid, *N*	Other solutions added	Observation
I a	0·2	Nil	Intense red colour immediately.
b	0·2	1 ml Na_2SO_4 10%	Faint red colour immediately; does not intensify even after 10 minutes.
c	0·2	2 ml Na_2SO_4 10%	Very faint red colour immediately; does not intensify even after 10 minutes.
d	0·2	5 ml Na_2SO_4 10%	No red colour within 5 minutes.
II a	0·5	Nil	Intense red colour immediately.
b	0·5	1 ml Na_2SO_4 10%	Very faint red colour almost immediately; does not intensify even after 10 minutes.
IIIa	1·0	Nil	Very faint red colour immediately; does not intensify with time; but addition of a trace of Ce^{IV} produces an intense red colour immediately.
b	1·0	5 ml ICl 0·005*M*	Red colour immediately.
c	1·0	5 ml Na_2SO_4 10%	Very faint red colour after one minute; no intensification of the colour with time; not intensified by a trace of Ce^{IV}.
d	1·0	5 ml Na_2SO_4 10%	Faint red colour in one minute; does not intensify with time.
e	1·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005*M*	Perceptible red colour in 30 secs; does not intensify with time.
f	1·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005*M* at 50°	Perceptible red colour in 15 secs; intensifies in 30 secs.
IVa	2·0	Nil	No red colour even after 5 minutes; addition of a trace of Ce^{IV} produces an intense red colour immediately.
b	2·0	5 ml ICl 0·005*M*	Red colour immediately.
c	2·0	5 ml Na_2SO_4 10%	No red colour even on addition of a trace of Ce^{IV}.
d	2·0	5 ml Na_2SO_4 10% at 50°	Faint red colour in two minutes; does not intensify with time.
e	2·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005*M*	Very faint red colour in 30 secs; does not intensify with time.
f	2·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005*M* at 50°	Perceptible red colour in 30 secs; intensifies in 45 secs.
V a	3·0	Nil	No red colour even after 5 minutes; addition of a trace of Ce^{IV} does not produce any red colour.
b	3·0	5 ml ICl 0·005*M*	Red colour in one minute.
c	3·0	Nil at 50°	No red colour; addition of ICl produces red colour immediately.
d	3·0	5 ml Na_2SO_4 10%	No red colour.
e	3·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005*M*	Perceptible red colour in 30 secs; does not intensify with time.
f	3·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005*M* at 50°	Perceptible red colour in 30 secs; intensifies in 60 secs.

Procedure

Place 5–10 ml of the oxalic acid solution (about 0·05*N*) in a conical flask, treat with 15 to 20 ml of concentrated hydrochloric acid and 20 ml of 0·5 molar barium chloride and dilute to 150–200 ml. Add 3–4 drops of 0·01*M* ferroïn, and titrate the mixture in the cold with 0·05*N* ceric sulphate solution. Titration can be carried out rapidly till about 99% of the oxalic acid is oxidised. At this stage add the oxidant dropwise and stir the solution for about 30 seconds. The disappearance of the red colour is noticed sharply enough, without any masking by the precipitated barium sulphate, if the total volume of the titration mixture is about 150–200 ml. The method has been found to work very satisfactorily even in the titration of 0·01*N* oxalic acid solutions.

Some typical results obtained in the determination of oxalic acid by the procedure now described are given in Table II.

In the titration of decinormal solutions of oxalic acid; it is desirable to dilute the reaction mixture to 300 ml to avoid masking of the red colour of ferroïn by the precipitated barium sulphate.

TABLE II.

Oxalic acid taken, *millimoles*	Oxalic acid found, *millimoles*
0·0250	0·0250
0·0500	0·0500
0·0800	0·0795
0·1000	0·0995
0·1500	0·1500
0·2000	0·1995
0·2500	0·2495

Acknowledgement—One of us (Dr. V. Panduranga Rao) desires to thank the Ministry of Education, Government of India, for the award of the National Research Fellowship.

Zusammenfassung—Der Beweis wurde, erbracht, dass, im Gegensatz zu der Auffassung früherer Autoren, die Reaktion zwischen Cerisulfat und Oxalsäure in salzsaurem Medium schnell verläuft, besonders, wenn Jodmonochlorid als Katalysator anwesend ist. Die Notwendigkeit, während der cerimetrischen Titration von oxalsäure die Temperatur der Lösung auf 50°C zu halten, ist nicht durch die langsame Reaktion zwishcen oxalsäure und Ce^{+4} bedingt, sondern vielmehr auf die langsame Reaktion zwischen Oxalsäure und oxydiertem Ferroin in Gegenwart von Sulfation (vom Cerisulfat stammend) zurückzufähren. Es wurden die Bedingungen gefunden um Oxalsäure mit Cerisulfat in 1 n Salzsäure bei Zimmertemperatur zu titrieren; Bariumionen werden zugesetzt um die Sulfationen abzufangen, die sowohl die Reaktion zwischen Oxalsäure und Ce^{+4} als auch die zwischen Oxalsäure und oxydiertem Ferroin stark verlangsamen. Die neue Methode hat mehrer Vorteile gegenüber der von Willard und Young beschriebenen. Die Temperaturerhöhung auf 50°C ist nicht nötig, was wichtig ist, da bei höherer Temperatur Ferroin ziemlich dissoziiert; ferner erübrigt sich Zugabe von Jodmonochlorid als Katalysator.

Résumé—Les auteurs montrent qu'il est évident que, contrairement aux conclusions des premiers chercheurs, la réaction entre le sulfate cérique et l'acide oxalique est très rapide en milieu acide chlorhydrique, spécialement en présence de monochlorure d'iode comme catalyseur. La nécessité d'une température de 50° dans le titrage cérimétrique de l'acide oxalique utilisant l'*o*-phénanthroline ferreuse comme indicateur n'est pas due à la lenteur de la réaction entre l'acide oxalique et le cérium (IV), mais à celle de la réaction entre l'*o*-phénanthroline ferreuse oxydée et l'acide oxalique en présence d'ion sulfate provenant du sulfate cérique. On a élaboré les conditions du titrage de l'acide oxalique par le sulphate cérique à la température ambiante en milieu acide chlorhydrique *N*, en utilisant l'*o*-phénanthroline ferreuse comme indicateur et l'ion baryum pour la précipitation de l'ion

sulfate, qui retarde notablement les deux réactions suivantes: acide oxalique -*o*.phénanthroline ferreuse et acide oxalique-Ce (IV). La méthode que les auteurs viennent de développer présente différents avantages sur celle prescrite par Willard et Young, puis-qu'elle évite la haute température de 50°, à laquelle on trouve que l'indicateur *o*-phénanthroline ferreuse subit une faible dissociation. Elle évite aussi l'utilisation de monochlorure d'iode comme catalyseur.

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PRELIMINARY COMMUNICATION

Some aspects of the polarographic behaviour of technetium and rhenium*

(*Received* 30 *May* 1959)

TECHNETIUM, element No. 43, was first obtained in 1937, by Perrier and Segré, by neutron-bombardment of a molybdenum target.[1] This is the method by which the main supply of the element available today has been obtained, but attempts have also been made[2] to extract workable amounts of technetium from the fission products of ^{235}U. Large quantities, however, are still not freely available for a complete investigation of its chemistry. Gerlit,[3] in a recent report on some chemical properties of the element, states that the chemical, and especially the analytical properties are comparatively little known.

A survey[4] of methods for the determination of technetium shows that the number of published methods is very small. Meggers[5] has suggested spectral lines suitable for the spectrographic determination of the element, and recently a colorimetric method based on thiocyanate has been reported.[6] Rulfs and Meinke[7] have determined the ultra-violet absorption spectrum.

In this laboratory, the amount of technetium available for study was originally about 30 micrograms, and later approximately 1 milligram. To carry out investigations on the analytical and general chemical behaviour of the element it was necessary to employ techniques requiring only very small amounts of the element. By means of ultramicro methods reagents for the detection[8] of Tc and for its separation from a number of associated elements and determination[9] have been developed. It was decided to investigate the oxidation-reduction behaviour of the element polarographically; and at the same time to examine rhenium as a control and a guide, since, as might be expected, work carried out in this laboratory on the separation of Tc from other elements indicated that its behaviour was much more similar to that of rhenium than to that of manganese. Other workers have drawn similar conclusions about its oxidation-reduction behaviour.[10]

A number of polarographic studies on rhenium have been reported.[11] As far as can be ascertained from the literature, no information on the polarographic behaviour of technetium has been published.† The results of the polarographic investigations are reported in this paper.

EXPERIMENTAL

Apparatus and solutions

Polarograms were determined using the conventional-type Tinsley Pen-Recording Polarograph. In some cases checks have been carried out using the Rapid-Sweep K1000 Southern Instruments Polarograph, but these results are not reported in the present paper.

To accommodate the small volume of solution, micro-cells with external calomel and silver electrodes were employed. De-aeration was carried out with argon. The dropping mercury electrode was calibrated and all measurements were made at 25° unless otherwise stated. All the values given for $E_{1/2}$ are with reference to the Standard Calomel Electrode. Technetium was present as pertechnetate, the solutions being $10^{-5}M$ in TcO_4^-.

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* This paper has been presented at a Joint Meeting of the Polarographic Society and the Scottish Section of the Society for Analytical Chemistry held in the Department of Chemistry, The Queen's University, Belfast on Friday 26 June 1959. Part of the material had previously been presented in preliminary form at a Joint Czech-Hungarian Polarographic Symposium held in Prague, Czechoslovakia in July 1958.

† After the announcement of the Meeting at which this paper was presented, the authors were kindly supplied by Dr. P. F. Thomason of the Oak Ridge National Laboratory with a copy of a paper dealing with work of a similar nature, to be presented by Dr. M. T. Kelley of that Laboratory at the 2nd International Congress of Polarography in Cambridge in August 1959.

The supporting electrolytes were as follows:

- (*a*) 12*N* H_2SO_4.
- (*b*) 2*N* KCl.
- (*c*) 2*N* NaOH.
- (*d*) 4*N* HCl.
- (*e*) 2*N* KOH buffered with sodium potassium tartrate.

RESULTS

(*a*) *In 12N H_2SO_4*

In the polarogram for pertechnetate there appeared to be a wave in the range from −0·3 volt to −0·8 volt, but this was not well formed. This is quite surprising, since in the reduction of perrhenate ion under the same conditions three well-defined waves were found. If the acid strength in the perrhenate solution was less than 8*N*, two waves only appeared.

The oxidation states to which the rhenium waves refer were observed visually by microscopic examination of the region in the vicinity of the mercury cathode, and yellow-orange and black products were found to form. On the basis of this examination it is suggested that the mechanism of reduction of perrhenate in sulphuric acid solution is as follows:

$$Re^{+7} + 3e^- \rightarrow Re^{+4}$$
$$Re^{+4} + 4e^- \rightarrow Re^0$$

In 8*N* H_2SO_4 the wave obtained at $E_{1/2} = -0{\cdot}8$ volt was found to be ideal for the determination of rhenium occurring as perrhenate, and details will be published elsewhere.[12]

(*b*) *In 2N KCl*

The polarogram showed two waves. The first has a value $E_{1/2} = -0{\cdot}65$ volt and the second $E_{1/2} = -1{\cdot}30$ volt. Under the same conditions of reduction perrhenate showed waves at $E_{1/2} = -1{\cdot}1$ volt and $E_{1/2} = -1{\cdot}7$ volt.

To decide the oxidation states to which Tc^{VII} and Re^{VII} were reduced use was made of the Ilkovic equation. This may be written in the form

$$\frac{i_d}{c} = 607nD^{1/2}m^{2/3}t^{1/6}$$

where

i_d = diffusion current,
c = concentration
n = number of electrons transferred,
D = diffusion coefficient in cm^2/sec,
m = weight of mercury in mg/sec,
t = drop time in sec.

For the pertechnetate wave at $E_{1/2} = -0{\cdot}65$ volt, with the following values: $i_d = 0{\cdot}2\ \mu A$; $c = 10^{-2}$ m*M*; $m^{2/3}t^{1/6} = 2{\cdot}40$; the value for n was found to be $\simeq 3$. This would indicate the reduction

$$Tc^{+7} + 3e^- \rightarrow Tc^{+4} \qquad (E_{1/2} = -0{\cdot}65 \text{ volt})$$

The second wave, occurring at $E_{1/2} = -1{\cdot}30$ volt rises to a maximum and then falls rapidly. Because of the nature of the wave it was not possible to apply calculations, but it is suggested that it might represent initial reduction to Tc^- followed by a reaction at the mercury surface. For the perrhenate reduction at $E_{1/2} = -1{\cdot}1$ volt calculations gave n = 8 indicating the reaction

$$Re^{+7} + 8e^- \rightarrow Re^-$$

i.e. the formation of rhenide as found by Lingane.[13]

(*c*) *2N NaOH*

In the pertechnetate solution a clearly defined step occurs at $E_{1/2} = -0{\cdot}85$ volt with the indication of a second step at $E_{1/2} = -1{\cdot}0$ volt. Under similar conditions per-rhenate shows a wave at $E_{1/2} = -1{\cdot}1$ volt.

Calculations from the Ilkovic equation indicate the transfer of 3 electrons for pertechnetate at $E_{1/2} = -0{\cdot}85$ volt:

$$Tc^{+7} + 3e^- \rightarrow Tc^{+4}.$$

The second wave again (as in the case of the $2N$ KCl solution) rises to a maximum and then falls off rapidly.

For rhenium the wave at $E_{1/2} = -1{\cdot}1$ volt also indicates a three-electron transfer:

$$Re^{+7} + 3e^- \rightarrow Re^{+4}.$$

(*d*) *In 4N HCl*

For pertechnetate two waves are obtained at $E_{1/2} = -0{\cdot}15$ volt and $E_{1/2} = -0{\cdot}35$ volt. There is also an indication of a third wave starting at $-0{\cdot}7$ volt. Under the same conditions per-rhenate shows waves at $E_{1/2} = -0{\cdot}1$ volt and $E_{1/2} = -0{\cdot}8$ volt.

(*e*) *In buffered 2N KOH*

The pertechnetate solution shows a well-defined wave at $E_{1/2} = -0{\cdot}65$ volt, and there is an indication of a second wave at $E_{1/2} = -1{\cdot}2$ volt. This solution was investigated in order to provide a comparison with manganese, where three waves are obtained[14] at $E_{1/2} = -1{\cdot}1$ volt, $E_{1/2} = -1{\cdot}3$ volt and $E_{1/2} = -1{\cdot}7$ volt.

The technetium wave at $-0{\cdot}65$ volt is well-defined, and promises to be suitable for the determination of technetium down to low concentration. This aspect is at present being studied.

A complete examination of all the reductions described here is being carried out with the rapid-sweep polarograph, and will be reported in due course.

Acknowledgement—We are indebted to the United Kingdom Atomic Energy Authority for facilities for separating small amounts of technetium from fission-product waste, and to U.K.A.E.A. and Professor R. S. Nyholm, University College, London for their loan of 1 milligram of technetium which was of great value in permitting confirmation of the preliminary results obtained on ultramicro quantities.

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DISCUSSION

Mr. Tyrrell: Is it the intention to use the K1000 Polarograph to detect unstable intermediate valency states of technetium?

Dr. Magee: Yes. Some investigations have been carried out, but these are not yet complete enough to give a full picture of the reductions.

Mr. Tyrrell: Is any work on rhenium and manganese reported in which the K1000 Polarograph has been used?

Dr. Magee: No investigations on rhenium or manganese using this instrument appear to have been reported in the literature. As a guide to the behaviour of technetium we, however, have carried out investigations, particularly on rhenium.

Mr. Tyrrell: You say that in $2N$ KOH manganese goes from the VII state to the II state. Are there intermediate states?

Dr. Magee: Yes. Three waves occur which indicate the following reduction steps: VII → IV: IV → III: III → II. Similar results have been reported in the literature by other workers.

Mr. Faircloth: Why do you use the Ilkovic equation to calculate n, and therefore assume a value for the diffusion coefficient?

Dr. Magee: The Ilkovic equation was used because, for rhenium, D_{ReO_4} had been determined. Until the exact value for D_{TcO_4} was determined, however, an approximate value based on that for rhenium indicated the order of n. I do agree, however, that from the shape of the plot E vs. $\log \frac{i_d - i}{i_d}$, n could also have been obtained.

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SHORT COMMUNICATIONS

The determination of tellurium in the presence of antimony in alloy amounts, using EDTA

(*Received* 6 *April* 1959)

AN existing turbidimetric method,[1] modified as follows, has been extended to the determination of tellurium in alloys containing antimony.

Procedure

To 1 g of Te-Sb-Pb alloy add 50 ml of concentrated hydrochloric acid containing bromine, and leave until dissolved. Expel bromine by boiling, and make up to 100 ml with hydrochloric acid (2 : 1). Take a 25-ml aliquot of this solution, evaporate to 2-3 ml, and add 5 ml of 10% EDTA solution, 6 ml of 4% gum arabic solution and 40 ml of water. Dissolve any precipitate by heating, and add 5 ml of a solution of 32 g of sodium hypophosphite in 100 ml of 1 : 1 hydrochloric acid. Heat for 15 min, cool, and adjust to pH 1–2 with 0·88 ammonia solution. Make up to 100 ml and measure the optical density at 435 mμ. The error is 4–5%.

REFERENCE

[1] R. A. Johnson and B. A. Anderson, *Analyt. Chem.* 1955, **27**, 120.

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Der Einfluss von Phosphorsäure auf die Uranbestimmung mit Ammoniumthiocyanat

(*Received* 12 *June* 1959)

CURRAH und Beamish[1] und vor kurzem Javanović und Zucker,[2] haben den Einfluß von Salz-, Salpeter- und Schwefelsäure auf die Farbbildung des Urans nach der Thiocyanatmethode wie sie von Nelson und Hume[3] beschrieben wurde, studiert. Sie fanden daß die Säuremenge genau bekannt sein muß, um die Resultate reproduzieren zu können. Der Einfluß der Phosphorsäure war nur bis 20 mg/ml untersucht worden, eine Konzentration bei der noch kein Einfluß bemerkt werden konnte. Da beabsichtigt war, in eigener Arbeit die Urankonzentration bei höherer Phosphorsäurekonzentration zu messen, wurde der Einfluß von Phosphorsäure auf die Farbbildung untersucht.

Es wurde gefunden, daß die Farbeintensität mit zunehmende Säurekonzentration abnimmt, wie in Tabelle I und Fig. 1 gezeigt ist.

Daneben zeigt es sich noch, daß die Farbe bei den höheren Phosphorsäurekonzentration sehr unbeständig ist und schon nach kurzer Zeit einen rötlichen Ton annimmt. Blanklösungen die kein Uran enthalten, zeigen ebenfalls einen rötlichen Ton bei höheren Phosphorsäurekonzentrationen wenn sie gegen dest. Wasser gemessen werden, wie in Tabelle II und Fig. 2 gezeigt ist.

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Der Einfluss von Phosphorsäure auf die Uranbestimmung mit Ammoniumthiocyanat

(*Received* 12 *June* 1959)

CURRAH und Beamish[1] und vor kurzem Javanović und Zucker,[2] haben den Einfluß von Salz-, Salpeter- und Schwefelsäure auf die Farbbildung des Urans nach der Thiocyanatmethode wie sie von Nelson und Hume[3] beschrieben wurde, studiert. Sie fanden daß die Säuremenge genau bekannt sein muß, um die Resultate reproduzieren zu können. Der Einfluß der Phosphorsäure war nur bis 20 mg/ml untersucht worden, eine Konzentration bei der noch kein Einfluß bemerkt werden konnte. Da beabsichtigt war, in eigener Arbeit die Urankonzentration bei höherer Phosphorsäurekonzentration zu messen, wurde der Einfluß von Phosphorsäure auf die Farbbildung untersucht.

Es wurde gefunden, daß die Farbeintensität mit zunehmende Säurekonzentration abnimmt, wie in Tabelle I und Fig. 1 gezeigt ist.

Daneben zeigt es sich noch, daß die Farbe bei den höheren Phosphorsäurekonzentration sehr unbeständig ist und schon nach kurzer Zeit einen rötlichen Ton annimmt. Blanklösungen die kein Uran enthalten, zeigen ebenfalls einen rötlichen Ton bei höheren Phosphorsäurekonzentrationen wenn sie gegen dest. Wasser gemessen werden, wie in Tabelle II und Fig. 2 gezeigt ist.

Tabelle I.—Der Einfluß von Phosphorsäure auf die kolorimetrische Bestimmung des Urans mit Ammoniumthiocyanat.

H_3PO_4 *M*	Optische Absorption*		
	0,1 *mg U/ml*	0,2 *mg U/ml*	0,4 *mg U/ml*
1	10,0	19,0	29,0
2	7,5	13,5	21,5
4	5,0	12,5	19,5
8	6,0	10,5	18,0

* Farbe gemessen gegen Blanklösung

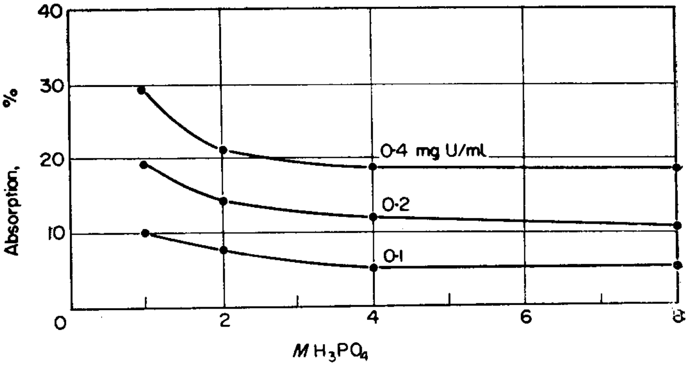

Fig. 1.—Der Einfluß von H_3PO_4 auf die kolorimetrische Bestimmung des Urans mit Ammoniumthiocyanat.

Tabelle II.

H_3PO_4 *M*	Optische Absorption* der Blanklösungen
1	5,0
2	5,5
4	6,0
6	6,5
8	11,0

* Farbe gemessen gegen dest. Wasser

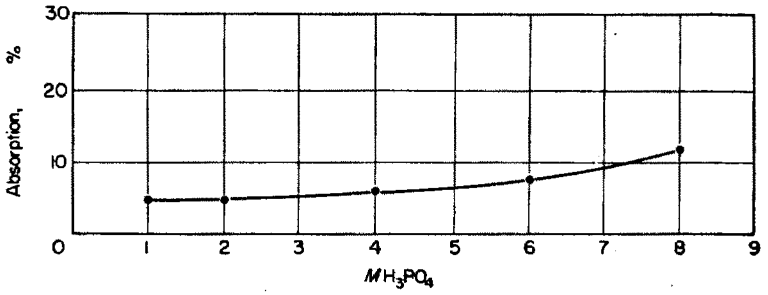

FIG. 2.—Optische Absorption der Blanklösungen.

Gemessen wurde in Lange-Kolorimeter mit Blaufilter sofort nach Zusatz der Reagenzien. Für die Uranbestimmung bei diesen Phosphorsäurekonzentrationen, muß die Phosphorsäure vor der kolorimetrischen Bestimmung abgetrennt werden.

LITERATUR

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[2] V. S. Javanović und E. F. Zucker, *Bull. Inst. Nucl. Sc. "Boris Kidrich,"* 1954, **69**, 111.

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The improved preparation of sulphatoceric acid for preparation of standard titrimetric solutions

(*Received* 18 *June* 1959)

PROBABLY the most frequent difficulty met with in popularizing the use of sulphatoceric acid as a standard oxidant involves the preparation of the solution of Ce^{IV} in sulphuric acid without the troublesome appearance upon standing of an insoluble residual cerium compound.

Ceric hydroxide, $Ce(OH)_4$, when properly prepared eliminated this difficulty entirely.

PREPARATION OF CERIC HYDROXIDE

Add a saturated solution of ammonium nitratocerate, $(NH_4)_2Ce(NO_3)_6$, in water to an excess of reagent ammonia, sp.gr. 0.90, diluted with an equal volume of water, and stir vigorously. Ceric hydroxide, $Ce(OH)_4$, is quantitatively precipitated in readily filterable form. Filter precipitate, and wash it free of ammonia and ammonium nitrate. Air dry this precipitate, requiring two to three weeks. Do not carry the dehydration lower than that which corresponds to the formula $Ce(OH)_4$ preferably leaving 2 to 3% unremoved moisture. Grind the horny product thus obtained to pass a 100-mesh sieve.

PREPARATION OF SULPHATOCERIC ACID IN SULPHURIC ACID

Place 10.4 g of $Ce(OH)_4$ in a dry 800-ml beaker. Add 50 ml of reagent sulphuric acid. Stir well, best with a magnetic stirring rotor. Now add slowly 150 ml of water. In 30 to 60 seconds the solution will be clear and reddish-orange in colour. If a minute insoluble portion remains, added heat with stirring is required. Dilute to 650–750 ml with water, transfer to a 1000-ml graduated flask and dilute to the mark. An approximately 0.05 normal solution of Ce^{IV} which is 0.75 formal in sulphuric

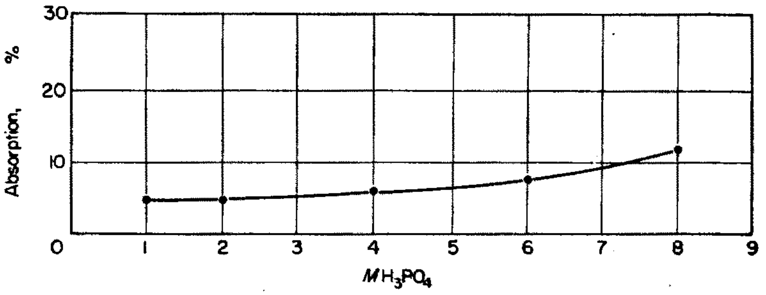

FIG. 2.—Optische Absorption der Blanklösungen.

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This quality of $Ce(OH)_4$ is available commercially and one pound will prepare more than 40 litres of approximately 0.05 normal solution at a cost of less than 20 cents (1s 6d) per litre.

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Metal complexes of N:N:N′:N′ tetrakis-(2-hydroxypropyl)-ethylenediamine

(*Received* 16 *June* 1959)

THE structural similarity of N:N:N′:N′-tetrakis-(2-hydroxypropyl)-ethylenediamine,* THPED (Figure 1), to ethylenediaminetetraacetic acid, EDTA, suggests that THPED may form complexes of analytical interest similar to those formed by EDTA.

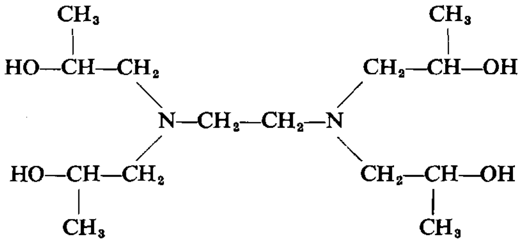

Fig. 1. N:N:N′:N′-Tetrakis-(2-hydroxypropyl)-ethylenediamine

TABLE I.—N:N:N′:N′-TETRAKIS-(2-HYDROXYPROPYL)-ETHYLENEDIAMINE METAL ION COMPLEXES

Cation	Complex	K_f	D_1	D_2	Colour
Cu^{++}	$Cu(THPED)^{++}$	$2{\cdot}6 \times 10^{9}$	$8{\cdot}8 \times 10^{-7}$	$6{\cdot}3 \times 10^{-10}$	blue
Ni^{++}	$Ni(THPED)^{++}$	$7{\cdot}1 \times 10^{6}$	$3{\cdot}2 \times 10^{-10}$	—	blue
Zn^{++}	$Zn(THPED)^{++}$	$2{\cdot}2 \times 10^{5}$	$5{\cdot}0 \times 10^{-8}$	$1{\cdot}0 \times 10^{-9}$	colourless
Cd^{++}	$Cd(THPED)^{++}$	$4{\cdot}2 \times 10^{7}$	$3{\cdot}2 \times 10^{-11}$	—	colourless
Pb^{++}	$Pb(THPED)^{++}$	$3{\cdot}1 \times 10^{7}$	$5{\cdot}0 \times 10^{-7}$	$8{\cdot}0 \times 10^{-11}$	colourless
Co^{++}	$Co(THPED)^{++}$	$5{\cdot}0 \times 10^{5}$	$4{\cdot}5 \times 10^{-8}$	$1{\cdot}3 \times 10^{-10}$	purple
Hg^{++}	$Hg(THPED)^{++}$	$1{\cdot}2 \times 10^{8}$	$1{\cdot}0 \times 10^{-7}$	$4{\cdot}0 \times 10^{-11}$	colourless
Ag^{+}	$Ag(THPED)^{+}$	$2{\cdot}4 \times 10^{4}$	—	—	colourless

Constants were determined at 27°, ionic strength $\mu = 0{\cdot}05$. THPED complexes of Ni^{+2} and Cu^{+2} have been previously reported by Hall *et al.*[1]

A survey of common metal cations (Fe^{+3}, Fe^{+2}, Cr^{+3}, Hg^{+2}, Cd^{+2}, Al^{+3}, Bi^{+3}, Pb^{+2}, Zn^{+2}, UO_2^{+2}, Sn^{+2}, Mg^{+2}, ZrO^{+2}, Ba^{+2}, Ca^{+2}, Sr^{+2}, Co^{+2}, Ag^{+}, Cu^{+2}, Ni^{+2}, Pt^{+4}, Ce^{+4}, Ce^{+3} and Th^{+4}) showed that Ag^{+}, Pb^{+2}, Hg^{+2}, Cu^{+2}, Cd^{+2}, Co^{+2}, Ni^{+2} and Zn^{+2} were sequestered by THPED. The formation constants, K_f, were estimated by potentiometric titrations. The complexes showed acidic properties; and where the acidity was titratable in aqueous solutions with $0{\cdot}1N$ NaOH potentiometrically, first (D_1) and second (D_2) acid dissociation constants were estimated (Table I).

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* N:N:N′:N′-tetrakis-(2-hydroxypropyl)-ethylenediamine is commercially available from Wyandotte Chemicals Corporation, Wyandotte, Michigan, under the registered trademark "QUADROL."

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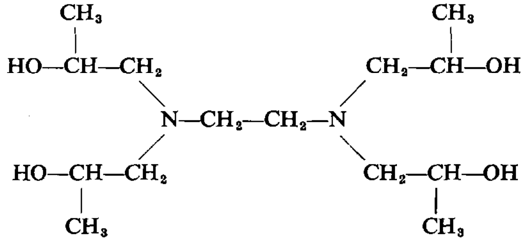

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THPED is a colourless liquid amine, miscible with water in all proportions. It is commercially available at low cost. THPED solutions are readily standardized acidimetrically. THPED shows more selectivity than EDTA in formation of metal complexes. These chemical and physical properties of THPED suggest possible uses in compleximetry, as masking agent or a titrant, and as a colorimetric analytical reagent.

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REFERENCE

[1] J. L. Hall, F. R. Jones, C. E. Delchamps and C. W. McWilliams, *J. Am. Chem. Soc.* (1957), **79**, 3361.

Notes on the reduction of nitrates

(*Revised communication received* 16 *May* 1959)

THERE are many papers dealing with the reduction of nitrates,[1] but very few which consider the mechanism of the reduction. In connection with our new nitrate determination described elsewhere[2] we have examined this problem.

EXPERIMENTAL

(a) First an attempt was made to measure the effectiveness of the reduction with various metals. To a known amount of sodium nitrate (1 millimole) was added an equivalent amount of the well-powdered metal, the same sulphuric acid concentration and temperature being used in all cases. Using metals with a range of standard potentials (Ni, Cd, Fe, Zn, Al, Ti) iron was found to be the most effective reducing agent although its standard potential lies in the middle of the series. It was shown also that using a stoichiometric amount of the metal, reduction is not complete even in the case of iron ("*ferrum reductum*); this reduced nitrate ions to ammonia to an extent of 87%.

(b) The lowest limit of the amount of iron which produces complete reduction of 1 millimole of nitrate was investigated; 1·5 g of iron is sufficient for this purpose. Other metals must be added in much greater amounts for complete reduction.

(c) Finally an attempt was made to reduce the amount of iron needed for complete reduction. Some catalysts are very effective and in the presence of these the amount of iron can be reduced substantially. Results of these experiments are shown in Table I. In the presence of 0·3 g of cupric copper, nickel or cobaltic salt, 0·5 g metallic iron is sufficient for quantitative reduction of 1 millimole of nitrate ion. It is quite obvious that metals are deposited from the solution on the surface of iron and the effectiveness of this mixed catalyst is much greater than that of iron. To use Co or Ni salts is convenient from other aspects too; metallic Co or Ni, which is formed, was dissolved in the sulphuric acid present and so the determination could be carried out in homogenous medium.

DISCUSSION

According to these results complete reduction of nitrate to ammonia can be carried out only when iron is present. Using other metals a negative error occurs in all cases due to losses (some intermediate products, such as nitrogen dioxide, nitrous acid, nitric oxide or nitrogen are volatile). Moderate amounts of iron prevent the formation of volatile products, although the reduction takes place in several steps, as it was shown by Acworth and Armstrong.[3] Complete reduction of nitrate ions needs 8 electrons:

$$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$$

but one atom of metallic iron produces only 2 electrons:

$$Fe = Fe^{2+} + 2e^-$$

THPED is a colourless liquid amine, miscible with water in all proportions. It is commercially available at low cost. THPED solutions are readily standardized acidimetrically. THPED shows more selectivity than EDTA in formation of metal complexes. These chemical and physical properties of THPED suggest possible uses in compleximetry, as masking agent or a titrant, and as a colorimetric analytical reagent.

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TABLE I.—REDUCTION OF NITRATE WITH METALLIC IRON IN THE PRESENCE OF VARIOUS METAL SALT CATALYSTS

NaNO$_3$ taken,	Catalyst,	0·1*N* HCl consumed by the ammonia,	Average consumption,	NaNO$_3$ found,	Difference	
mg	*g*	*ml*	*ml*	*mg*	*mg*	%
85·51		8·60 8·77 8·94	8·77	74·54	−0·97	−13·0
	0·50CuSO$_4$·5H$_2$O	10·05 10·06 10·04	10·05	85·42	−0·09	−0·1
	0·50NiSO$_4$·7H$_2$O	10·05 10·06 10·05	10·05	85·42	−0·09	−0·1
	0·50CoSO$_4$·7H$_2$O	10·03 10·09 10·04	10·04	85·34	−0·17	−0·2
	0·50Cr$_2$(SO$_4$)$_3$·18H$_2$O	9·39 8·28 8·84	8·83	75·05	−10·46	−12·3
	0·50Na$_2$MoO$_4$·2H$_2$O	5·59 5·84 6·05	5·82	49·47	−36·04	−42·4

The oxidation number of nitrogen alters in stages so that N^{+5}, N^{+3}, N^{+1}, N^{-1}, N^{-3} are formed. Corresponding ions to these oxidation states are shown in Fig. 1. It may be seen from this scheme that the oxidation states N^{+4}, N^{+2} and N^{0}, corresponding to the volatile products NO_2, NO and N_2 respectively, are missing. Thus volatile nitrogen compounds can be formed only by secondary reactions.[4] Among these the following reactions can occur:

$$3HNO_2 = HNO_3 + 2NO + H_2O \tag{1}$$

$$2HNO_2 = N_2O_3 + H_2O \tag{2}$$

$$H_2N_2O_2 = N_2O + H_2O \tag{3}$$

$$HNO_2 + NH_3 = N_2 + 2H_2O \tag{4}$$

$$HNO_2 + H_2NOH = N_2O + 2H_2O \tag{5}$$

$$HNO_2 + HNO_3 = 2NO_2 + H_2O \tag{6}$$

$$HNO_3 + NH_3 = N_2O + 2H_2O \tag{7}$$

The rate of reaction (3), which is the decomposition of hyponitrous acid, is very small in strongly acidic dilute solution[5] and therefore it is impossible to show the presence of nitrous oxide in the gases after reduction by metals. Reaction (7) takes place only in non-aqueous media when temperature is raised above 150°C. The remaining possibilities (1, 2, 4–6) are concerned with the decomposition of free nitrous acid. It was possible to detect nitrous acid by the Griess–Ilosvay reagent in all the reductions[6,7] except those carried out with metallic iron. An attempt to detect nitrite ions in the presence of iron$^{\text{II}}$ ions with the Griess–Ilosvay reagent was unsuccessful. It was possible to establish that on adding a dilute nitrous acid to an iron$^{\text{II}}$ sulphate solution the pH of the solution increases somewhat. Nitrous acid may therefore form a stable complex with iron^{II} ions, probably according to equation (8)

$$[Fe(H_2O)_6]^{2+} + HNO_2 = [Fe(H_2O)_5NO]^{3+} + OH^- + H_2O \qquad (8)$$

It is possible that nitroprusside complex is formed from hexacyanoferrate^{II} ions and nitrous acid by reaction (9) as follows:

$$[Fe(CN)_6]^{4-} + HNO_2 \rightleftarrows [Fe(CN)_5NO]^{2-} + OH^- + CN^- \qquad (9)$$

This reaction is analogous to the reaction (8), the only difference being that in the latter NO^+ ions displace cyanide ions instead of water molecules from the inner sphere of the complex. Displacement of cyanide ions is accompanied by less decrease of free energy than the decomposition of the aqueous complex since the stability constant of the former is much greater than that of the latter. Thus, the exceptional function of iron during the reduction of nitrate ions can be explained by the fact that the nitrous acid which is primarily formed reacts with iron^{II} ions (which are also products of the reaction) giving a stable complex in an acidic solution. There is therefore no possibility of decomposing the nitrous acid or of reaction between the latter and other products of the reduction forming nitrogen or nitrogen oxides.

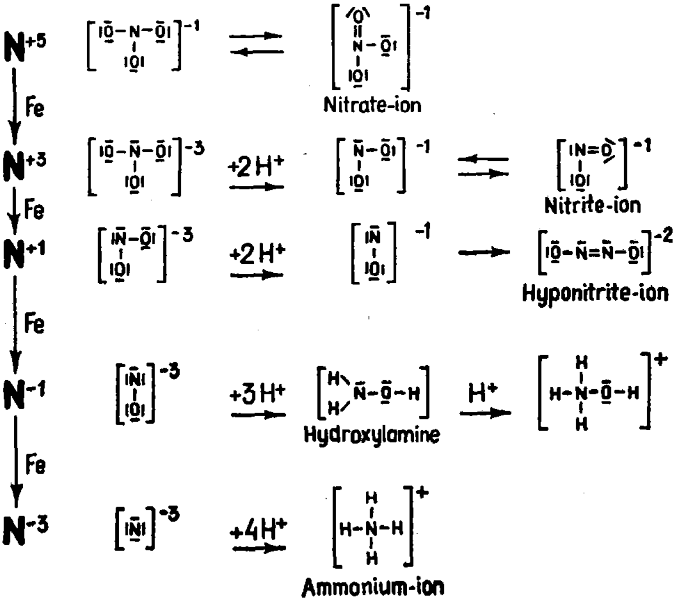

FIG. 1.

When, however, some traces of nitrogen oxides are formed during the reaction, they react with iron^{II} sulphate (which is present in the solution owing to the reduction) forming nitroso-iron^{II} sulphate. The latter reacts, as Tribalat suggested,[8] with nitrous acid instantaneously. We are of the opinion that the product of this reaction is also $[Fe(H_2O)_6NO]^{3+}$, and so the presence of iron^{II} sulphate assures that all nitrogen formed having oxidation number +2 or +4 is transformed into a complex containing nitrogen with oxidation number +3. When nitrous acid is bound to a complex, the reaction goes readily without side reactions through N^{+1} and N^{-1} to ammonia.

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Komplexometrische Bestimmung von Bor neben Barium

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Bei der Wärmebehandlung von Werkzeugen aus Werkzeug-oder Schnellstahl werden vielfach Salzbäder verwendet, die neben viel Bariumchlorid einen geringen Anteil an Borax oder Borverbindungen enthalten.

Nach Angaben von Gautier und Pignard[2] ist es möglich, die Borsäure als Bariumborotartrat $Ba_5B_2C_{12}H_8O_{24}H_2O$ zu fällen. Das Bariumborotartrat ist sehr schwer löslich und eignet sich sowohl zu einer gravimetrischen quantitativen Halbmikrobestimmung der Borsäure, als auch zum qualitativen mikrochemischen Nachweis. Der qualitative Nachweis ist bis zu einer Grenzkonzentration von $1 \cdot 10^{-5}$ möglich, wobei 5 mg Bor erkennbar sind.

Gautier und Pignard bestimmen den Borgehalt bei ihren Analysen nach diesem Verfahren entweder durch Auswägen des bei 110° getrockneten Niederschlages oder durch jodometrische Titration des Bariums des Barium-borotartrates nach vorheriger Umsetzung mit Kaliumbichromat. Die mitgeteilten Beleganalysen für Mengen von 0,03–1 mg Bor zeigen Abweichungen von $\pm 3\%$.

Das Grundprinzip der neuen Methode beruht darauf, dass mit einer bekannten Bariummenge das Bor gefällt wird und im Filtrat der Überschuss an Barium mit Komplexon III bestimmt wird. Bei der direkten Titration des Bariums kann Phthaleinpurpur als Indikator verwendet werden. Es ist aber auch möglich, die Bariumbestimmung nach der Methode von Ballczo und Doppler[1] unter Verwendung eines Mischindikators auszuführen. Hierbei wird das gesamte Barium erst an Komplexon III gebunden und der Überschuss an ÄDTA mit genau eingestellter Magnesiumsalzlösung zurücktitriert.

Die Rücktitration der überschüssigen ÄDTA in Gegenwart von Bariumkomplexonat mit einer genau eingestellten Magnesiumchloridlösungberuht auf der Tatsache der sehr kleinen Komplexbildungskonstante des Bariums gegenüber Eriochromschwarz T und der äusserst starken Komplexbildung des Magnesiums mit diesem Farbstoff. Es ist daher unmöglich, das Barium aus seinem Komplexonkomplex durch Magnesiumionen bei Gegenwart von Eriochromschwarz T zu verdrängen, trotzdem der Magnesiumkomplexonatkomplex praktisch eine Zehnerpotenz stärker ist als der entsprechende Bariumkomplexonatkomplex.

$$\begin{array}{lccccccc} & \text{Mg Erio} & + & \text{BaH}_2\text{Y} & \rightleftharpoons & \text{MgH}_2\text{Y} & + & \text{BaErio} \\ \log K & 7{,}0 & & 7{,}76 & & 8{,}69 & & 2 \end{array}$$

Aus dieser Gleichung ist zu ersehen, dass die Reaktion von links nach rechts nicht ablaufen kann, da das Produkt der Komplexbildungskonstante auf der linken Seite um einige Zehnerpotenzen grösser ist als auf der rechten Seite. Ein weiterer Vorteil bei der Rücktitration ist darin noch zu sehen, dass keine Komplexumbildung erfolgen muss und der erste Überschuss an Magnesiumionen sofort den festen Eriochromschwarz T-Komplex bildet und der bekannte Farbumschlag erfolgt. Nach Ballczo und Doppler wurde diese Methode noch insofern verbessert, dass sie an Stelle von Eriochromschwarz

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Komplexometrische Bestimmung von Bor neben Barium

(*Received* 14 *May* 1959)

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TABELLE I.—ABSCHLIESSEND SOLLEN NOCH EINIGE VERSUCHSERGEBNISSE MITGETEILT WERDEN

Nr.	Borax		Bor		Verbr. ml 0,01 m ÄDTA		% Fehler
	gegeb. *mg*	gef. *mg*	err. *mg*	gef. *mg*	gef.	err.	
1	16	16,020	1,8155	1,818	2,100	2,097	+0,12
2	11	10,910	1,2480	1,238	1,430	1,420	−0,91
3	8	8,010	0,9078	0,9089	1,050	1,049	+0,12
4	5,6	5,569	0,6354	0,6319	0,730	0,734	−0,55
5	2,8	2,746	0,3177	0,3116	0,360	0,367	−1,93
6	1,6	1,602	0,1816	0,1818	0,210	0,2097	+0,12
7	0,8	0,788	0,0908	0,0892	0,103	0,1049	−1,50

T folgenden Mischindikator verwenden: 1 g Tropäolin OO, 2 g Eriochromschwarz T und 500 g NaCl.

Auf Grund der von mir durchgeführten Versuche haben sich folgende Arbeitsvorschriften zur Bestimmung von Borsäure in bariumhaltigen und bariumfreien Salzen und Lösungen am besten bewährt:

Verwendete Lösungen und Reagenzien

1. Fällungsreagenz für bariumfreie Salze:

   13 g Bariumchlorid, krist.
   14 g Weinsäure
   240 g Ammoniumchlorid
   } in 1 Liter dest. Wasser lösen

2. Fällungsreagenz für bariumhaltige Salze:

   14 g Weinsäure
   240 g Ammoniumchlorid
   } in 1 Liter dest. Wasser lösen

Vor der Fällung wird dem verwendeten Fällungsreagenz 1/10 seines Volumens konz. Ammoniak (D. 0,910) zugesetzt.

3. 0,01–0,1 m Komplexon-III-Lösung (Dinatriumsalz der Äthylendiamintetraessigsäure).
4. 0,01–0,1 m Magnesiumchloridlösung.
5. Phthaleinpurpur 0,1 %ige alkoholische Lösung.
6. Mischindikator: 1 g Tropäolin OO
   2 g Eriochromschwarz T
   500 g Natriumchlorid p.a.
   werden fein verrieben.
7. Bariumchlorid p.a.
8. Borax und Borsäure p.a.
9. Puffer pH 10: 54 g NH$_4$Cl, 350 ml NH$_3$ (D. 0,910) auf 1 l. Wasser.

Arbeitsvorschrift für bariumfreie Salze

0,1 g bis 1 g Substanz werden in 100 ml destilliertem Wasser gelöst. 10 ml dieser Lösung sollen 0,1–3 mg Bor enthalten und werden mit dem mit Ammoniak versetzten Fällungsreagenz bis zur 100 ml Marke aufgefüllt. Nach 2 Std. wird durch ein trockenes Filter filtriert. 10 ml des Filtrates pipettiert man in einen 100 ml Messkolben, füllt mit dest. Wasser bis zur Marke auf und pipettiert 25 ml ab.

(a) Bei der direkten Titration und Verwendung von Phthaleinpurpur als Indikator werden die 25 ml mit 10 ml conc. Ammoniak, 15 ml dest. Wasser und 50 ml Alkohol verdünnt, einige Tropfen der alkoholischen Indikatorlösung zugegeben und sofort mit Komplexon III-Lösung titriert.

(b) Bei der indirekten Titration unter Verwendung des oben beschriebenen Mischindikators werden

15 ml 0,01 m Komplexonlösung, 20 ml Pufferlösung und ca. 30 mg des Mischindikators zugegeben und mit 0,01 m Magnesiumchloridlösung von blaugrün über grau auf rot titriert.

Bei dem Blindversuch werden 10 ml dest. Wasser mit dem Fällungsreagenz bis zur 100 ml Marke aufgefüllt und dann weiter wie oben beschrieben verfahren.

Da zur Ausfällung von 2 Mol. Borsäure 5 Mol. Bariumchlorid und zur Umsetzung von 1 Mol. Borax sogar 10 Mol. Bariumchlorid benötigt werden, entspricht

1 ml 0,01 m Komplexonlösung = 0,04328 mg Bor
1 ml 0,01 m Komplexonlösung = 0,38143 mg Borax ($Na_2B_4O_7$) 10 HO_2

Arbeitsvorschrift für bariumhaltige Salze

10 g Salz genau abgewogen werden in dest. Wasser gelöst und die Lösung bis zur 100 ml Marke aufgefüllt. Lösung 1: 10 ml dieser Lösung werden in einen Messkolben pipettiert und mit dem Fällungsreagenz 2 bis zur Marke aufgefüllt. Nach 2 Std. wird dann wie oben beschrieben weiter verfahren.

Der Blindversuch wird folgendermassen durchgeführt: 10 ml der Lösung 1 werden in einem 100 ml Messkolben mit destilliertem Wasser bis zur Marke aufgefüllt und dann, wie bereits beschrieben, weiter verfahren. Der Verbrauch an Komplexon III kann hierbei gleich auf $BaCl_2$ umgerechnet werden. Es ist also möglich, in einer Einwaage neben dem Borax-Gehalt auch gleich ben Bariumchloridgehalt zu bestimmen.

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Semi-micro determination of silicon and phosphorus in organic compounds

(*Received* 30 *May* 1959)

No method applicable when both silicon and phosphorus were present in a compound has been mentioned in recent reviews of methods for the determination of silicon[1,2] and phosphorus[3,4] in organic compounds. In the analysis of silicon in rocks, Brabson *et al.*[5] precipitated phosphorus with the silicon and corrected for the phosphorus content; and Wilson[6] prevented co-precipitation of silicate with phosphate without separation when analysing fertilisers.

It is, perhaps, relevant to note here that, during some preliminary experiments, it was found that silicon could not be determined in the presence of phosphorus-containing materials by simple wet oxidation of the organic material in a platinum crucible followed by weighing the silica produced. Very high results were obtained.

In order to permit analysis of some high-boiling liquids containing silicon and phosphorus, two semi-micro methods used in our laboratory for the determination of phosphorus have been modified to allow the determination of phosphorus and silicon on one individual sample.

Acid digestion method

The method of Belcher and Godbert[7]—digestion with nitric and sulphuric acids followed by gravimetric determination of phosphate after precipitation with Jörgensen's reagent—although shown not to be universally applicable,[8] had given satisfactory results for the determination of phosphorus in a variety of organic compounds. It was established that, after acid digestion of compounds containing silicon and phosphorus, the phosphate-containing acid liquid could be quantitatively separated from the silica precipitated in the glass boiling tube by use of an elongated

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In order to overcome this difficulty, a reasonably non-hygroscopic form of silica was prepared by removing the digestion liquid and then washing the residue with nitric acid (1 + 1) followed by alcohol. The residue was then dried at 100° under reduced pressure, cooled in a desiccator and weighed. The majority of this silica was then tipped into a platinum crucible, weighed, ignited to bright red heat and weighed again. The correction factor (weight after ignitition/weight of silica ignited) was applied to the original total weight of silica in the boiling tube and the silicon content calculated from this corrected figure.

TABLE I

Compound	% Si calculated	% Si found	% P calculated	% P found
$C_{22}H_{32}N_2O_3Si_2$	13·09	13·22		
		13·18		
		13·14		
		12·94		
$C_{26}H_{60}O_9P_2Si_2$	8·84	8·50	9·75	9·75
		8·52		9·76
$C_{38}H_{52}O_9P_2Si_2$	7·28	7·17	8·04	7·80
		7·49		7·80
		7·53		7·78
		7·59		

The results obtained for the analysis of three research compounds (one not containing phosphorus) by this method are shown in Table I.

Peroxide bomb method

The second, and more universally successful, method[8] used in our laboratory for phosphorus determination involves decomposition of the organic material (in a micro bomb) with sodium peroxide followed by precipitation of phosphate in the acidified bomb leachings as quinoline phosphomolybdate. Co-precipitation of silicomolybdate could be avoided by complexing with citric acid[6] or by removal of the silicon[8] by volatilisation as tetrafluoride or precipitation as silica. The latter procedure was found to provide a means for the determination of silicon.

The normal procedure for the determination of phosphorus[8] was followed except that the acidified bomb leachings were evaporated to dryness and baked at 110°. After cooling, the crystals were moistened with concentrated hydrochloric acid, dried and baked again. The soluble salts were dissolved in hot water and filtered through a paper-pulp pad, the filtrate and washings being collected in a conical flask for precipitation of phosphate in the usual way. All the insoluble residue was collected on the paper pad during the filtration and the whole was quantitatively transferred into a platinum crucible. The paper was ashed and the residue was weighed, treated with hydrofluoric acid and reweighed. From the loss in weight, the silicon content of the organic material was calculated.

Results obtained for the analysis of three organic compounds are shown in Table II. A gravimetric finish[9] for the determination of phosphorus was used.

Discussion

From the limited number of samples available, both methods have produced results which are within the normally accepted limits (±0·3 %) for organic analysis but it is considered that the procedure following peroxide bomb fusion is superior, being manipulatively simpler, more precise and, probably, more universally applicable.

TABLE II

Compound	% Si calculated	% Si found	% P calculated	% P found
$C_{14}H_{36}O_9P_2Si_2$	12·03	11·81 11·91	13·28	13·16 13·18
$C_{26}H_{60}O_9P_2Si_2$	8·84	8·68 8·74	9·75	9·72 9·75
$C_{38}H_{52}O_9P_2Si_2$	7·28	7·15 7·15	8·04	8·00 7·99

Both methods suffer from the disadvantage that the conversion factor for silicon ($Si/SiO_2 = 0{\cdot}4672$) is poor, requiring a sample containing at least 2·5 mg of silicon to provide a reasonable weight of silica for determination. Precipitation as the silicomolybdate of an organic base[10–12] might provide a better means for determining silicon after separation from phosphate.

Interference in the determination of silicon by fluoride, after mineralisation in the peroxide bomb, can be overcome by the addition of boric acid to the bomb leachings before acidification.

Acknowledgements—We are indebted to Mr. E. J. P. Fear and Dr. I. M. White for the provision of samples, and to Mrs. M. W. Roberts for experimental work on the acid digestion procedure.

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LETTERS TO THE EDITOR

Ion-exchange separation from alcoholic medium

SIR:

The great value of analytical separation of metals in solution by anion-exchange from hydrochloric acid solution is now firmly established. Kraus and Moore have studied the distribution coefficients of most metals as a function of aqueous hydrochloric acid concentration. Working at General Electric Research Laboratory and at Iowa State, we have discovered independently that anion-exchange separations in the system hydrochloric acid–water–alcohol offer great versatility. One group (G.E.) used ethyl alcohol, and the other (Iowa State) uses *iso*propyl alcohol.

The distribution coefficients for most metals are significantly higher in systems containing an appreciable quantity of alcohol. This makes a partly nonaqueous medium especially valuable for retention of metals, such as copper^{II} and manganese^{II}, which have low distribution coefficients in aqueous hydrochloric acid solution. Also, most metals are strongly taken up by anion-exchange resins at a much lower hydrochloric acid concentration in alcohol–water than in water alone. The altered exchange behaviour of metals in partly alcoholic medium permits some separations which are not possible in aqueous hydrochloric acid. Detailed papers concerning analytical aspects of ion-exchange separations from alcoholic medium will be forthcoming.

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17 *July* 1959

Precipitation of nickel dimethylglyoximate from homogeneous solution by direct synthesis of the organic reagent

SIR:

Although metal chelates, *e.g.* nickel dimethylglyoximate and aluminium 8-hydroxyquinolinate can be precipitated from homogeneous solution by raising the pH through the hydrolysis of urea,[1,2] there have been but few and only recently reported methods involving the synthesis *in situ* of the organic chelate reagent. For example, Tarasevich[3] has precipitated copper and silver with 1H-benzotriazole synthesized by reacting nitrous acid and *o*-phenylene-diamine, and Heyn and Brauner-have precipitated cobalt with 1-nitroso-2-naphthol synthesized by reacting nitrous acid and 2-naphthol.

We have been able to precipitate nickel^{II} from homogeneous solution with dimethylglyoxime generated by reacting biacetyl with hydroxylamine in aqueous solution under controlled conditions; the chelate is precipitated in the form of red needles. The results of this investigation, which includes the synthesis of other oximes, will subsequently be reported in *Talanta*. (Note: At the time this note was written, Ramette[5] reported to us that he has precipitated nickel dimethylglyoximate as long red needles of the order of 2 mm in length by the replacement method.[6] Ramette uses a slight excess of EDTA to complex nickel^{II} in the presence of dimethylglyoxime and then adds zinc ions which slowly replace the nickel ions, thus effecting precipitation of nickel dimethylglyoximate.)

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SIR:

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We have been able to precipitate nickel^{II} from homogeneous solution with dimethylglyoxime generated by reacting biacetyl with hydroxylamine in aqueous solution under controlled conditions; the chelate is precipitated in the form of red needles. The results of this investigation, which includes the synthesis of other oximes, will subsequently be reported in *Talanta*. (Note: At the time this note was written, Ramette[5] reported to us that he has precipitated nickel dimethylglyoximate as long red needles of the order of 2 mm in length by the replacement method.[6] Ramette uses a slight excess of EDTA to complex nickel^{II} in the presence of dimethylglyoxime and then adds zinc ions which slowly replace the nickel ions, thus effecting precipitation of nickel dimethylglyoximate.)

Department of Chemistry and Chemical Engineering E. D. SALESIN
Case Institute of Technology LOUIS GORDON
Cleveland 6, *Ohio, U.S.A.*
29 *July* 1959

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[1] E. L. Bickerdike and H. H. Willard, *Analyt. Chem.*, 1952, **24**, 1026.
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[4] A. H. A. Heyn and P. A. Brauner, paper presented at 135th meeting of American Chemical Society, Boston, Mass., 1959.
[5] R. W. Ramette, Department of Chemistry Carleton College, Northfield, Minnesota, U.S.A., personal communication.
[6] L. Gordon, M. L. Salutsky and H. H. Willard, *Precipitation from Homogeneous Solution*, John Wiley and Sons, Inc., New York, 1959.

Talanta, 1959, Vol. 2, p. 394. Pergamon Press Ltd. Printed in Northern Ireland

TALANTA MEDAL

The Publishers of TALANTA, Pergamon Press Limited, have generously offered to provide the funds for the institution and award, from time to time, of a TALANTA Medal. This Medal will be awarded for outstanding contributions to analytical chemistry, and will have a value of 100 guineas.

CONDITIONS OF AWARD

1. The TALANTA Medal will be awarded for really outstanding contributions to analytical chemistry made by scientists in any area of research endeavour.

2. Any outstanding paper or papers contributed to TALANTA will automatically be considered for the Medal. Other work may be proposed by any member of the Advisory Board of TALANTA to the Editors for consideration. The award will not be confined to current work, but may be made for work already completed which has since been recognised as outstanding.

3. The Medal will only be awarded on the unanimous recommendation of a committee composed of the Editor-in-Chief, the Regional Editors, and the Chairman of the Advisory Board. In addition, the recommendation must be supported by at least two-thirds of the members of the Advisory Board. Although normally the TALANTA Medal will not be awarded more frequently than once in each year, no attempt will be made to award it at fixed intervals.

Talanta, 1959, Vol. 2, pp. 395 to 399. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Precipitation from Homogeneous Solution. LOUIS GORDON, MURRELL L. SALUTSKY and HOBART H. WILLARD. John Wiley and Sons, Inc., New York: Chapman and Hall, Limited, London, 1959. pp. viii + 187. 60s. $7.50.

FOR a number of years the reviewer has used the field of precipitation from homogeneous solution as a very effective example to show that vital developments in "classical" analysis are still possible. It is therefore to him a particular pleasure to welcome this account of the subject by authors whose names are so closely associated with the field and who have done so much to develop it.

After a brief introductory chapter, the book goes on to deal with the main categories of compound which can be precipitated from homogeneous solution—hydroxides and basic salts, phosphates, oxalates, sulphates, sulphides and miscellaneous compounds. In all of these chapters the general principles are discussed, and then detailed procedures for the analytical applications of the technique are given. These chapters therefore give an excellent account, compact but comprehensive, of the use of the technique in analytical chemistry.

If the book stopped at this point it would be a useful contribution to the practice of analytical chemistry, but would fail to bring out some of the most important implications of the technique. However, the next two chapters, dealing with co-precipitation and fractional precipitation, are a welcome contribution to the theory of precipitation, and at the same time an admirable account of the way in which this new technique has contributed (and is capable of further contribution) to our knowledge of that complex phenomenon, precipitation, about which, after effectively centuries of use, so much still is not understood. These two chapters, and in particular the former, should stimulate a considerable amount of thought about an everyday procedure which is too often taken for granted.

A final chapter discusses the application of the principles of precipitation from homogeneous solution to several regions of chemical technology—separation processes, the production of reproducible carriers for radioactive products, and other materials not otherwise readily manufactured. This emphasises the fact that a field which is often thought of as purely analytical has much wider applications.

The book, as would be expected by anyone who knows the authors and their contributions to analytical chemistry, is pleasantly written, concise, and easy to read. It is a valuable survey of this field at a time when the literature is becoming sufficiently extensive to require it, and it will be found indispensable to all analytical chemists dealing (and which of them does not?) with precipitation processes. As would be expected from the publishers' imprint, the production is above criticism.

If the reviewer may, in the end, be permitted to utter one very gentle reproach, it is that the authors have succumbed to the all too prevalent practice of using "data" when they mean "results".

CECIL L. WILSON

EDTA Titrations. An Introduction to the Theory and Practice. H. FLASCHKA. Pergamon Press, London, 1959. Pp. 138. 42s.

EDTA is now established as an analytical reagent, not merely for water hardness determination by the Schwarzenbach procedure, but as one of the most widely-used and versatile of organic compounds in the whole field of analytical chemistry. A glance through an index of the 1500 or so papers which have now appeared on this single topic shows that, with the possible exception of a rare metal or two,

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If it is not a very long-felt want (for the major development of the subject has been within the past five years) the need of a teaching manual on the analytical uses of EDTA has certainly become keenly-felt. This lacuna Professor Flaschka, whose wide teaching and research experience render him particularly well fitted for the task, has now most ably filled. As its title implies, his book has, probably wisely, been restricted in scope to titrimetric methods, and does not refer to the use of EDTA as a masking agent in gravimetric analysis and so forth. The brief theoretical treatment with which it opens is of exceptional clarity and there is included a discussion of the more important metallochromic indicators and of potentiometric and photometric methods of end-point determination. Full instructions, with the more important references to the literature, are given for the determination of most of the common metals and of a few representative mixtures of cations, and in the course of these the various ways in which EDTA can be used as a titrant are well exemplified. The use of masking agents and of indirect methods such as those for determining phosphate and halogens are also described. Above all, this is a *practical* book, the short chapter dealing with the possible reasons for the failure of a method in practice being of particular value. The reviewer's only important criticism is, in fact, purely one of economics: the price of 42s. is surely far too high for so comparatively small and specialised a book which is, moreover, primarily intended for students.

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HIDING under the simple title of *Trace Analysis* this book may, at first meeting, convey the idea that it is a textbook of qualitative methods for the detection of small amounts of metals, or just another book on spot tests. A study of the contents, or even a quick glance at the "Foreword" will, however, soon dispel this idea and reveal that it has a *raison d'être* and is something new in the field of trace constituents. It is a report of papers presented at a Symposium on Trace Analysis held at the New York Academy of Medicine in November 1955. The Symposium itself was the outcome of a general feeling that, despite the importance of trace elements in chemistry, medicine, biology, industry, etc., the subject had not received the co-operative effort it deserved as a unified field of science.

In soil chemistry, as catalytic agents in chemical processes, and in alloy steels, to mention only a few examples, trace elements have important effects on the qualities and behaviour of the whole material. Although the discovery of the function of the trace element is in the hands of the soil chemist, the enzyme chemist or the metallurgist, it is the analytical chemist whose job it is to demonstrate the presence and quantity of the element.

The number of ways in which the above objectives can be achieved may amaze some and surprise many for, in this book there are 24 contributions by authors, many of whom are internationally well-known, on topics which cover the whole field of analytical chemistry and part of what is sometimes regarded as the realm of physical chemistry.

After a brief introduction by one of the editors, the book is divided into three parts. Part I comprises 20 chapters under the general heading of "Methodology". The first chapter by H. H. Strain deals with the use of Chromatography and Electrochromatography in trace analysis. This is followed by chapters on Ion Exchange (K. A. Kraus); Extraction (L. C. Craig); Chemical Microscopy (W. C. McCrone); Spot Tests (F. Feigl and P. W. West); Colorimetry (M. G. Mellon); Fluorometry (C. E. White); Flame Spectrometry (B. L. Vallee); Potentiometry (N. H. Furman); Coulometry (L. B. Rogers); Polarography and Voltammetry (P. Delahay); Amperometry (C. N. Reilley); Emission Spectrochemical Analysis: Basic Principles and Applications (L. W. Strock); Emission Spectrochemical Analysis: Determination of Trace Elements in Plants and other Biological Material (R. L. Mitchell); γ-Ray Spectroscopy (H. W. Koch); Mass Spectroscopy (M. G. Inghram); X-ray Spectroscopy (T. Hall); X-ray Micrography (A. Engstrom); Neutron-Activation Analysis (A. A. Smales); Microbiological Techniques: Inorganic Ions (E. E. Snell).

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The complete work is, of course, quite outside the reach of the private individual, but no scientific library which aims to be well equipped can afford to be without them. In addition, individual volumes may well be expected to have such constant use as to make them a desired possession for the individual analytical chemist or at least for the analytical laboratory, so that they may be more readily available for frequent consultation. Optical rotatory power has, perhaps, a limited application, but the number of fields of modern chemistry which can make use of the most reliable and up-to-date information on oxidation-reduction potentials is nowadays legion.

The volumes are attractively and very sturdily bound, and should stand up well to the excessive amount of handling to which they may expect to be subjected. Some comment is perhaps called for about the lack of uniformity in the presentation of the title on the cover: in one of the present volumes this in English, in another in French, and in the third is given in both languages.

Annotated Bibliography of α-Benzildioxime. CHARLES V. BANKS, MICHAEL J. MAXIMOVICH, NELSON J. FOWLKES and PETER A. BEAK. United States Atomic Energy Commission, Research and Development Report ISC 1038. 1958. pp. 60, $1.75.

THIS booklet contains 150 references, covering the period from 1883 to 1956, dealing with α-benzildioxime, together with summaries of the contents of each reference. It is not restricted to the analytical uses of the material, but covers all aspects of its chemistry and application.

It is available from the Office of Technical Services, U.S. Department of Commerce, Washington, 25, D.C., U.S.A.

Source Material for Radiochemistry. Sub-Committee on Radiochemistry, Committee on Nuclear Science. Publication No. 654, National Academy of Sciences, National Research Council, U.S.A. 1959, pp. 23.

THIS booklet contains some 60 references, with brief abstracts, to papers dealing with radiochemical topics or topics which may have some bearing on radiochemical problems. Many of these references are to documents, and the availability of each item is listed. Material up to early 1959 is included.

The booklet is available free of charge from the Division of Physical Sciences, National Research Council, National Academy of Sciences, 2101 Constitution Avenue, Washington, 25, D.C., U.S.A.

Zincon: Organic Chemical Reagents, Monograph No. 37. EILEEN A. JOHNSON and W. JABLONSKI. Hopkin and Williams, Ltd., 1959. pp. 6.

THIS little booklet deals with the detection and absorptiometric determination of zinc and mercury by zincon (2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene), and with the use of the reagent as an indicator in the complexometric determination of zinc. Detailed procedures are described, interferences are fully dealt with, and a bibliography of 14 references is supplied.

It may be obtained from Messrs. Hopkin and Williams Limited, Chadwell Heath, Essex, England.

The following publications have been received:

Oak Ridge National Laboratory, Analytical Chemistry Division, Annual Progress Report for period ending December 31, 1958; 3 March 1959, M. T. KELLEY and C. D. SUSANO, ORNL-2662, TID-4500 (14th Ed.) Pp. xiii + 100. $2.50.

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THESE valuable additions to chemical reference literature are produced under the aegis of the International Union of Pure and Applied Chemistry, and with the full co-operation of commissions and members of that body.

The complete work is, of course, quite outside the reach of the private individual, but no scientific library which aims to be well equipped can afford to be without them. In addition, individual volumes may well be expected to have such constant use as to make them a desired possession for the individual analytical chemist or at least for the analytical laboratory, so that they may be more readily available for frequent consultation. Optical rotatory power has, perhaps, a limited application, but the number of fields of modern chemistry which can make use of the most reliable and up-to-date information on oxidation-reduction potentials is nowadays legion.

The volumes are attractively and very sturdily bound, and should stand up well to the excessive amount of handling to which they may expect to be subjected. Some comment is perhaps called for about the lack of uniformity in the presentation of the title on the cover: in one of the present volumes this in English, in another in French, and in the third is given in both languages.

Annotated Bibliography of α-Benzildioxime. CHARLES V. BANKS, MICHAEL J. MAXIMOVICH, NELSON J. FOWLKES and PETER A. BEAK. United States Atomic Energy Commission, Research and Development Report ISC 1038. 1958. pp. 60, $1.75.

THIS booklet contains 150 references, covering the period from 1883 to 1956, dealing with α-benzildioxime, together with summaries of the contents of each reference. It is not restricted to the analytical uses of the material, but covers all aspects of its chemistry and application.

It is available from the Office of Technical Services, U.S. Department of Commerce, Washington, 25, D.C., U.S.A.

Source Material for Radiochemistry. Sub-Committee on Radiochemistry, Committee on Nuclear Science. Publication No. 654, National Academy of Sciences, National Research Council, U.S.A. 1959, pp. 23.

THIS booklet contains some 60 references, with brief abstracts, to papers dealing with radiochemical topics or topics which may have some bearing on radiochemical problems. Many of these references are to documents, and the availability of each item is listed. Material up to early 1959 is included.

The booklet is available free of charge from the Division of Physical Sciences, National Research Council, National Academy of Sciences, 2101 Constitution Avenue, Washington, 25, D.C., U.S.A.

Zincon: Organic Chemical Reagents, Monograph No. 37. EILEEN A. JOHNSON and W. JABLONSKI. Hopkin and Williams, Ltd., 1959. pp. 6.

THIS little booklet deals with the detection and absorptiometric determination of zinc and mercury by zincon (2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene), and with the use of the reagent as an indicator in the complexometric determination of zinc. Detailed procedures are described, interferences are fully dealt with, and a bibliography of 14 references is supplied.

It may be obtained from Messrs. Hopkin and Williams Limited, Chadwell Heath, Essex, England.

The following publications have been received:

Oak Ridge National Laboratory, Analytical Chemistry Division, Annual Progress Report for period ending December 31, 1958; 3 March 1959, M. T. KELLEY and C. D. SUSANO, ORNL-2662, TID-4500 (14th Ed.) Pp. xiii + 100. $2.50.

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Neutron Activation Analysis Methods for the Group VIII Elements. C. E. MILLER. ORNL-2715, 21 May 1959. Pp. viii + 108. $2.50.

Analysis of Uranium Solutions using Anion Exchange in Nitrate Media. O. A. VITA, C. F. TRIVISONNO and C. W. PHIPPS. A.E.C. Research and Development Report GAT-283, April 28 1959. Pp. 14. $0.50.

Ion Exchange-Spectrographic Determination of Arsenic and Phosphorus in River Water. R. KO. A.E.C. Research and Development Report HW-59008, 21 January 1959. Pp. 14. $0.50.

Precipitation of Manganese Dioxide. J. T. GRACE, H. E. HENRY and D. KARRAKER. A.E.C. Research and Development Report DP-346, December 1958. Pp. 10. $0.50.

Internal Standard Method of General Spectrographic Analysis. F. M. SMITH. A.E.C. Research and Development Report HW-59864, 9 April 1959. Pp. 16. $0.50.

These are all available from Office of Technical Service, Department of Commerce, Washington, 25, D.C., U.S.A.

Talanta, 1959, Vol. 2, pp. 400 to 401. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged:

Friday 25 *September* 1959: **Society for Analytical Chemistry,** North of England and Scottish Sections: *Water: Determination and Examination. Determination of Water:* Dr. J. H. THOMPSON, *Water Analysis as a Guide to Potability:* Mr. J. G. SHERRATT. *Determination of Radioactive Contaminants in Water:* Mr. G. E. EDEN. Central Hotel, Victoria Viaduct, Carlisle, England. 7.15 p.m.

Monday–Wednesday 26–28 *October* 1959. **Seventh Detroit Anachem Conference.** Memorial Conference Center, Wayne State University, Detroit, Michigan, U.S.A.

Enquiry regarding registration may be made from Mr. J. W. COMPTON, Research Department, Wyandotte Chemicals Corporation, Wyandotte, Mich., U.S.A.

On the Tuesday afternoon will be held the Anachem Award Session in honour of G. FREDERICK SMITH, Emeritus Professor, University of Illinois. At the Conference Dinner JOHN C. BAILAR, Jr., President of the American Chemical Society will be guest speaker.

Wednesday–Friday 4–6 *November* 1959: Analytical Groups of the New York and North Jersey Sections of the **American Chemical Society,** New York, Delaware Valley, New England and Baltimore–Washington Sections of the **Society for Applied Spectroscopy, Metropolitan Microchemical Society:** Eastern Analytical Symposium and Instrument Exhibit. Hotel New Yorker, New York City.

The meeting will consist of a series of 3-hour symposia of invited papers of extended length by experts in a number of fields of interest to analysts. The emphasis will be on recent developments in these specialities. Features of the meeting will include the Annual Medal Award of the Society for Applied Spectroscopy and the banquet address by Dr. W. F. MEGGERS of the National Bureau of Standards.

For further information about the meeting contact PAUL LUBLIN, Publicity Chairman, Sylvania Research Laboratories, Bayside, New York, U.S.A.

Monday 29 *February–Friday* 4 *March* 1960: Analytical Chemistry Group, Pittsburgh Section, **American Chemical Society** and **Spectroscopy Society of Pittsburgh:** Eleventh Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. Penn-Sheraton Hotel, Pittsburgh, Penna., U.S.A.

This will include symposia on Statistical Control of Laboratory Operations, Gas Chromatography Nuclear Magnetic Resonance, Molecular Fluorescence Spectroscopy, Application of Infra-red Spectroscopy to Trace Analysis, Applied Nucleonics, and X-Ray Fluorescence Spectroscopy. In addition, papers are invited in all fields of analytical chemistry and spectroscopy.

Authors planning to submit papers should note that the last date for receipt of abstracts is 15 October 1959.

Information regarding papers may be obtained from Mr. JAMES E. PATERSON, Program Chairman, The Pittsburgh Conference, Jones and Laughlin Steel Corporation, Graham Research Laboratory, Pittsburgh, 30, Penna., U.S.A.

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

The papers presented will be in a similar form to those presented at the 2nd Symposium on Gas Chromatography held in Amsterdam and will be classified under three headings:— 1. Theory: 2. Apparatus and Techniques: 3. Applications.

Those papers concerning the application of the technique must have some novel feature to warrant their inclusion in the programme. Authors who wish to submit papers must forward an abstract (250 words) to the Secretary by 31st October, 1959. Abstracts received after this date cannot be considered for inclusion.

Papers to be read will be chosen by an editorial committee and the authors will be informed before 14th November, 1959.

Those wishing to attend the Symposium should apply to the Secretary for registration forms which will be sent as soon as they are available. The fee for the Symposium and receptions will be about £4. *Secretary:* Mr. L. BREALEY, Boots Pure Drug Co. Ltd., Standards Department, Station Street, Nottingham, England.

The *B.S.I. News* announces, among others, the following revised British Standard:

B.S. 1016: *Methods for the analysis and testing of coal and coke*, Part 7: 1959: *Ultimate analysis of coke.* This deals with the determination of carbon, hydrogen, nitrogen and total sulphur in coke. (Price 7s. 6d.) Part 11: 1959: *Forms of sulphur in coal.* This deals with the determination of sulphate, pyritic and organic sulphur in coal. (Price 4s. 6d.)

Amendment slips have been issued for the following Standards: PD 3315: Amendment No. 1 to B.S. 1428, Part D1: 1952: *Burettes with pressure-filling device and automatic zero.*

PD 3334: Amendment No. 3 to B.S. 846: 1952: *Burettes and bulb burettes.*

PD 3385: Amendment No. 1 to B.S. 1428 Part 1: 1953: *Combustion boats, sheaths and contact stars for microchemical analysis.* This amendment includes an alteration to the title, which will now read *Combustion boats and sheath for microchemical analysis.*

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

EDITORIAL NOTE

Two further issues of TALANTA will be published before the end of this year in order to complete the six issues due for 1959.

At a recent editorial meeting the problems raised by the increasing number of papers of high quality submitted to the Journal were discussed. Up to the moment, in spite of printing difficulties, an average publication rate close to our aim of 3–4 months for long communications and 30–60 days for preliminary communications and letters to the Editor has been maintained. It was decided, however, that if an increased period between acceptance and publication was not to be imposed upon contributors, it would be necessary to go over to monthly publication. Therefore, as from 1st January 1960, TALANTA will be published monthly.

In spite of the greater number of pages thereby involved, subscription rates **per annum** to **private subscribers** will remain the same (5 guineas or $15.00).

The subscription rate **per volume** to **libraries and institutions** will remain the same (£6 or $17.00). Since the new production schedule will be at the rate of 3 volumes per year, the charge will therefore be £18 or $51.00 **per annum.**

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Talanta, 1959, Vol. 2, p 402. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

The Formal Oxidation Potentials of Substituted 1:10-Phenanthroline Ferrous Complexes of Low Solubility. The Preparation and Redox Potentials of the Vanadate-Vanadyl System of Potentiopoised Solutions. G. Frederick Smith and Wm. M. Banick, Jr. (27 *May* 1959).

A Gamma Absorptiometer for Laboratory Analysis of the Heavy Metals. W. L. Maddox and M. T. Kelley. (28 *May* 1959).

A Critical Study of the Precipitation of Ammonium Phospho-12-molybdate. Peter Cannon. (2 *June* 1959).

Der Einflus von Phosphorsäure auf die Uranbestimmung mit Ammoniumthiocyanat. Fathi Habashi. (12 *June* 1959).

Über das Verhalten von isolierten Einschlüssen auf Eisenwerkstoff bei hohen Temperaturen. Hanns Malissa. (15 *June* 1959).

Metal Complexes of N:N:N′:N′-Tetrakis-(2-hydroxypropyl)-ethylenediamine. D. A. Keyworth. (16 *June* 1959).

The Improved Preparation of Sulphatoceric Acid for Preparation of Standard Titrimetric Solutions. Harvey Diehl and G. Frederick Smith. (18 *June* 1959).

Quantitative Spectrochemical Analysis of Minor Elements in Silicates with Double Internal Standards. Hiroshi Hamaguchi, Rokuro Kuroda and Ryokichi Negishi. (8 *July* 1959).

The Application of the Cathode Ray Polarograph to the Analysis of Explosives, II. The Determination of Mercury Fulminate. J. Hetman. (9 *July* 1959).

Analytical Applications of Xylenol Orange, IV. A Spectrophotometric Study of the Ferric Xylenol Orange Complex. K. L. Cheng. (14 *July* 1959).

Nucleation and Precipitation of Silver Chloride from Homogeneous Solution. David H. Klein, Louis Gordon and Thomas H. Walnut. (17 *July* 1959).

The Precipitation Nucleus of Silver Chloride. David H. Klein, Louis Gordon and Thomas H. Walnut. (17 *July* 1959).

Dosage Colorimétrique du Soufre en Faibles Teneurs dans les Aciers, les Fers et Cobalts Purs. P. Tyou and L. Humblet. (20 *July* 1959).

Organic Analysis, XX. Microestimation of Blood Sugar with 5-Hydroxy-1-tetralone. Tsutomu Momose and Yosuke Ohokura. (21 *July* 1959).

A Comparison of the Alkali Methoxides in the High-Frequency Titration of Acids in Dimethylformamide. S. F. Ting, W. S. Jeffery and E. L. Grove. (22 *July* 1959).

Titration of Metal Oxinates with Potassium Methoxide. Elizabeth E. Underwood and A. L. Underwood. (20 *July* 1959).

Tesla-luminescence Spectra, I. The Spectra of Some Inorganic Gases. T. Given, R. J. Magee and C. L. Wilson. (28 *July* 1959).

Talanta, 1959, Vol. 2, p. 403. Pergamon Press Ltd. Printed in Northern Ireland

BOOKS RECEIVED

Source Material for Radiochemistry. Subcommittee on Radiochemistry, Committee on Nuclear Science. Publication No. 654, National Academy of Sciences, Washington, D.C., March 1959. pp. 23.

Monographien aus dem Gebiete der qualitativen Mikroanalyse, Edited by A. A. Benedetti-Pichler: **Volume I. Anorganische Qualitative Mikroanalyse.** H. Malissa and A. A. Benedetti-Pichler. Springer-Verlag, Wien, 1958. pp. vii + 333. £4 3s 6d: $11.65: DM 49—.

Zincon: Organic Chemical Reagents, Monograph No. 37. Eileen A. Johnson and W. Jablonski. Hopkin and Williams, Ltd., Chadwell Heath, Essex, England, 1959. pp. 6.

Comprehensive Analytical Chemistry, Volume I A. Classical Analysis. Edited by Cecil L. Wilson and David W. Wilson. Elsevier Publishing Company, Amsterdam: D. Van Nostrand Co., London and New York, 1959. pp. xix + 577. 105s.

Ionenaustauscher, Band I: Grundlagen. F. Helfferich. Verlag Chemie, Weinheim, 1959. DM 48—. pp. viii + 520.

Progress in Nuclear Energy, Series IX. Analytical Chemistry, Volume I. Edited by M. T. Kelley. Pergamon Press Limited, London, Paris and New York, 1959. pp. 372. £5 5s.

Advances in Inorganic and Nuclear Chemistry, Volume I. Edited by H. J. Emeleus and A. G. Sharpe. Academic Press Inc., New York. 1959. pp. xi + 449. $12.00

Fluorocarbons. M. Rudner. Rheinhold Publishing Corporation, New York. Chapman and Hall, London, 1958. pp. x + 238. 46s.

Fundamentals of High Polymers. O. Battista. Rheinhold Publishing Corporation, New York. Chapman and Hall, London, 1958. pp. vii + 140. 44s.

Electrophoresis: Theory, Methods and Applications. Edited by M. Bier. Academic Press, Inc., New York, 1959. pp. xx + 563. $15.00

Analytical Chemistry in Nuclear Technology: Specific Applications of Diverse Methods of Chemical Analysis. Second Gatlinburg Conference. U.S. Atomic Energy Commission, Technical Information Service. April 1959. Pp. vii + 298. $3.00.

Analytical Chemistry in Nuclear Technology: Instrumentation, Remote Control Techniques and Nucleonics. Second Gatlinburg Conference. U.S. Atomic Energy Commission, Technical Information Service. April, 1959. Pp. vi + 236. $2.50.

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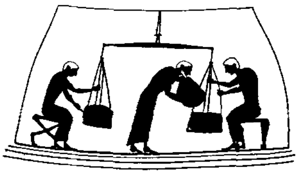

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(Names of authors of books reviewed are in italics)