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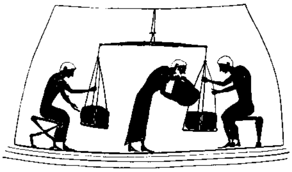

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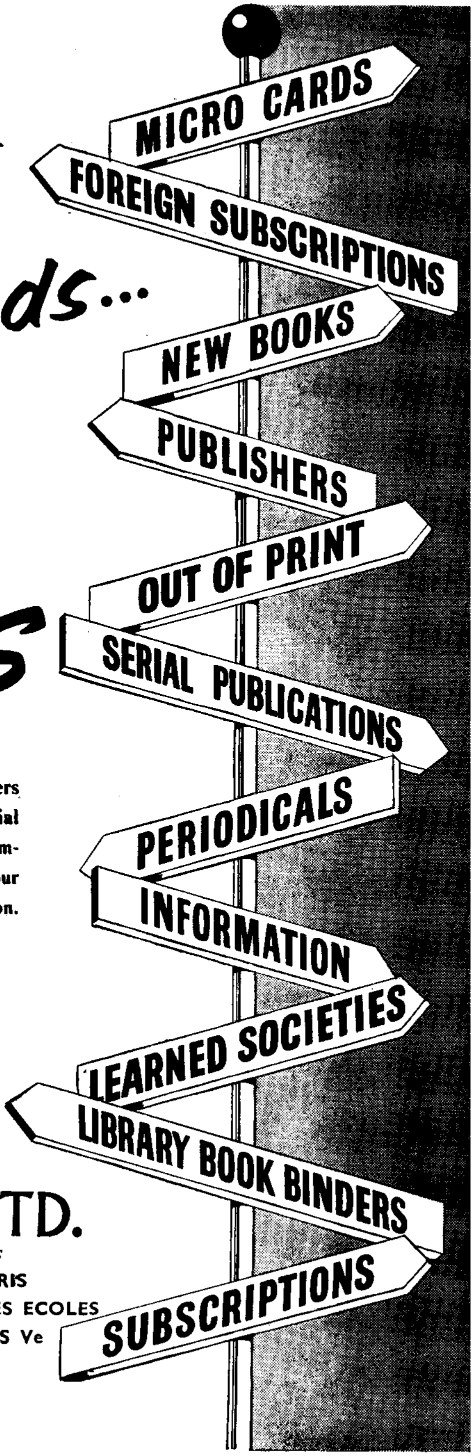
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DETERMINATION OF SMALL AMOUNTS OF COBALT IN TITANIUM, ZIRCONIUM AND THEIR ALLOYS

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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.
2·5	50	—	
2·5	5	5	Additional reagent added to test soln. and a compensating soln. containing vanadium used as blank.
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	3
		5	8
		20	22·5, 23, 23 23, 22·5, 22·5
2	Titanium + 4% Al + 4% Mn (314A alloy)	Nil	<2
		5	6
3	Titanium + 5% Al + 2·5% Sn (317 alloy)	Nil	2·5
		5	7·5
4	Titanium + 2·5% Al + 13% Sn (371 alloy)	Nil	3
		5	7·5
5	Titanium + 6% Al + 4% V (318A alloy)	Nil	<2
		5	6
6	Commercially pure zirconium	Nil	<2
		5	5·5
7	Zirconium + 1·5% Sn + 0·12% Fe + 0·1% Cr + 0·05% Ni (Zircaloy 2)	Nil	<2
		5	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 (.03*M*)

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 0.03*M* solution of copper and an approximately 0.03*M* 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 0.001*N* sodium hydroxide), and back-titrate under ultraviolet illumination with a standard copper solution (0.03*M*). 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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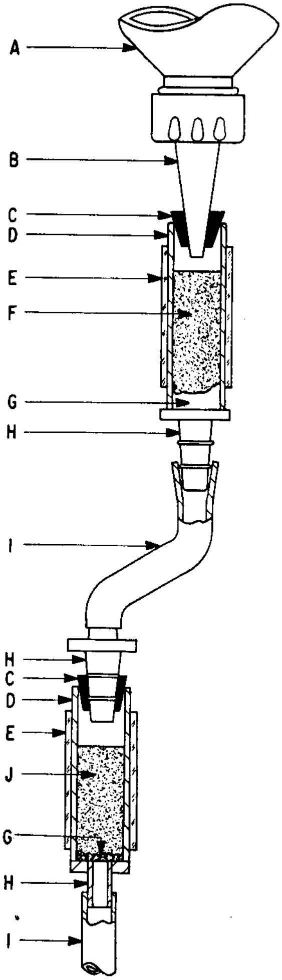

FIG. 1. Polyethylene ion-exchange columns in series

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 0.8*M* HF–0.06*M* 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 3*M* 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 4*M* 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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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 $1\cdot5 . 10^{-3}\%$ 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.

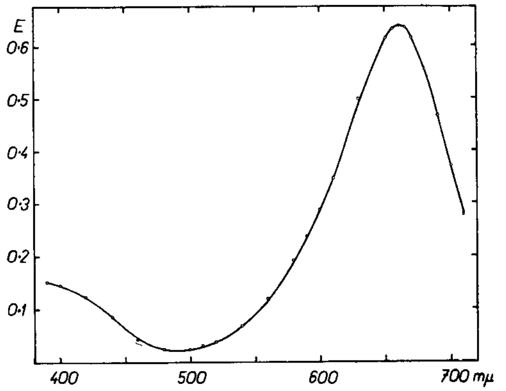

FIG. 1. Dependence of extinction upon wavelength.

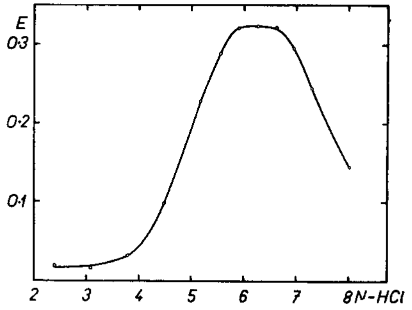

FIG. 2. Dependence of extinction upon acidity of the solution.

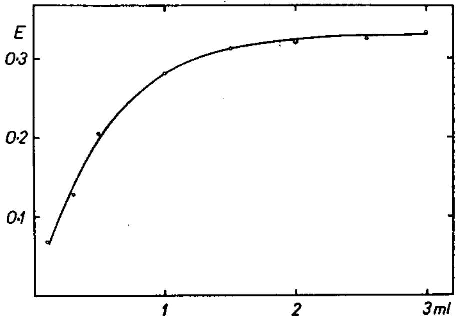

FIG. 3. Dependence of extinction upon amount of reagent added.

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 dbta, extraction-colorimetric methods with Malachite Green have been described only for thallium[6] 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.

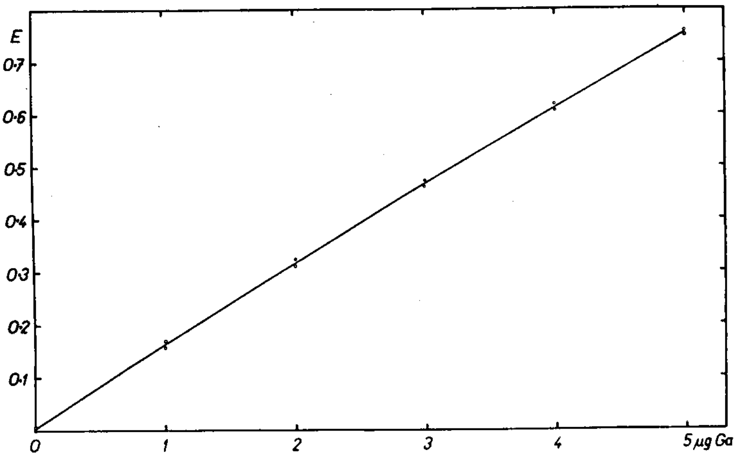

FIG. 4. Calibration curve of gallium with Malachite Green.

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

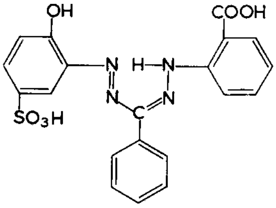
$$\underset{\text{Orange-Yellow}}{Ca^{2+} + HIn^{3-}} + ZnY^{2-} \rightarrow CaY^{2-} + \underset{\text{Blue}}{ZnIn^{2-}} + H^{+} \qquad (1)$$

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:

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

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

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

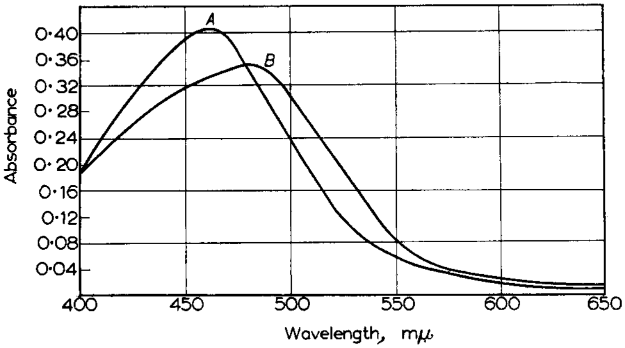


FIG. 1. Absorption spectra of free dye
A—2 × $10^{-3}M$ zincon in acetate buffer pH 5.9.
B—2 × $10^{-3}M$ zincon in triethanolamine buffer pH 10.0.

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 $0.001\,M$ 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 $(10^{-1 \cdot 95})$ 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.

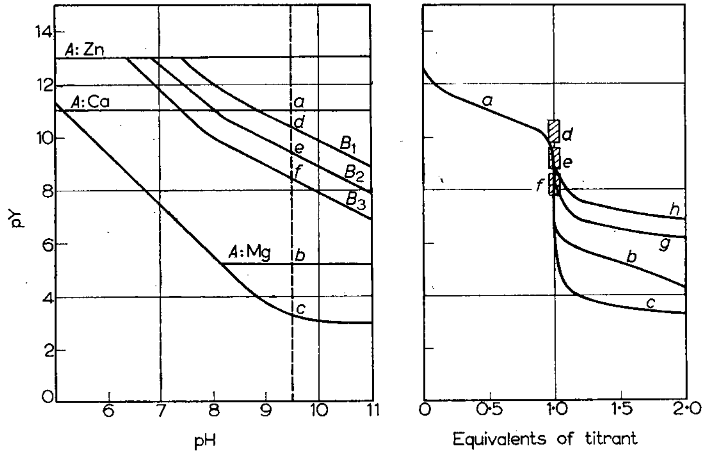


FIG. 2. pY–pH diagram and corresponding pY titration curve for the titration of $10^{-3}M$ calcium in the presence of magnesium with EGTA and zincon. Effect of buffer and hydrolysis of zinc disregarded. B_1, B_2 and B_3 correspond to Zn-EGTA in concentrations of 10^{-5}, 10^{-4} and $10^{-3}M$, respectively.

The lines in the diagram represent pY as a function of pH (pY $= -\log [\mathrm{Y}]$ 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.

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

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.

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

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

The $\mathrm{pY_B}$ at 50% colour change of the indicator is represented by line *B*

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

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.

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

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

[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 [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 cf 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

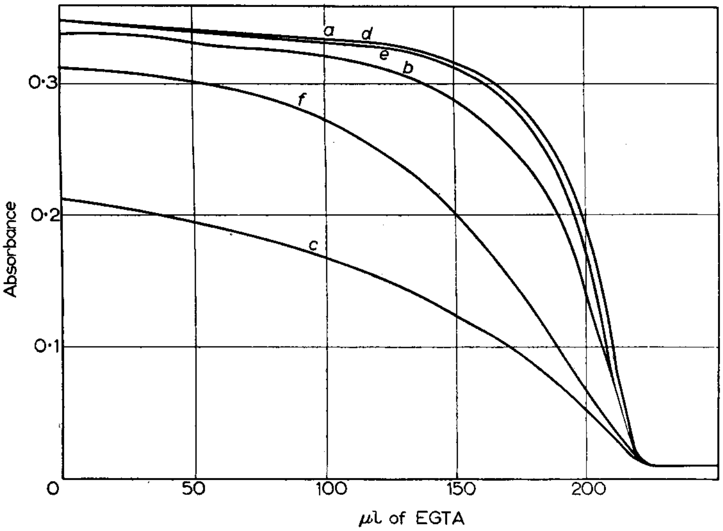


FIG. 3. Effect of buffer concentration. Spectrophotometric titration of 2.5×10^{-4} calcium with EGTA in the presence of $2.5 \times 10^{-4}M$ Zn-EGTA using zincon as indicator and different concentrations and types of buffers. *a*, *b*, and *c*: ammonia buffer pH 9.5, $10^{-3}M$, $10^{-2}M$ and $10^{-2}M$,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

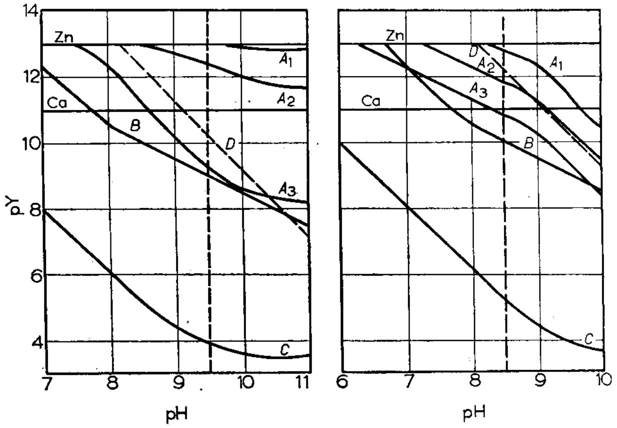


FIG. 4. Effect of buffer on titration of calcium 2.5×10^{-4} in the presence of and equal amount of Zn-EGTA. Left: ammonia buffer. Right: triethanolamine buffer. A_1 $0.001M$, A_2 $0.01M$, A_3 $0.1M$ buffer. B, 50% colour change of zincon. D, hydrolysis of zinc (oblique dashed line).

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).

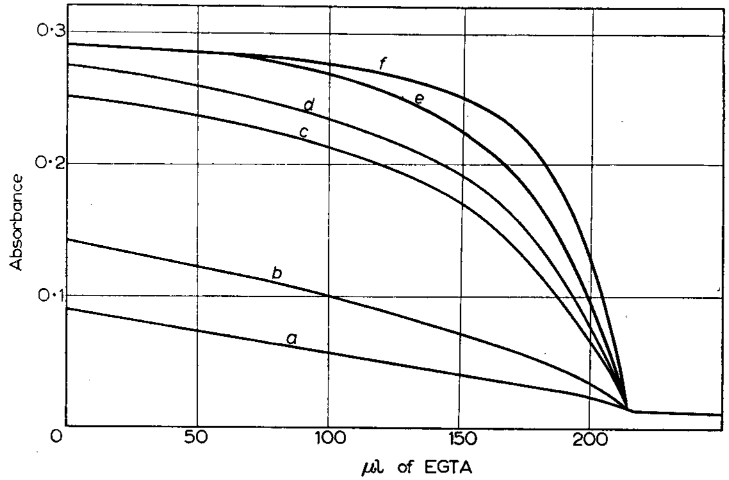


FIG. 5. Effect of concentration of Zn-EGTA. Titration of $2.5 \times 10^{-4}M$ calcium in $5 \times 10^{-3}M$ ammonia buffer. 1 ml $2 \times 10^{-3}M$ zincon. Concentration of Zn-EGTA: a- $5 \times 10^{-6}M$, b- $1 \times 10^{-6}M$, c- $2.5 \times 10^{-5}M$, d- $5 \times 10^{-5}M$, e- $1 \times 10^{-4}M$, 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 $2M$ 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), $0.2M$. 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 $2M$ 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 $1M$ 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.

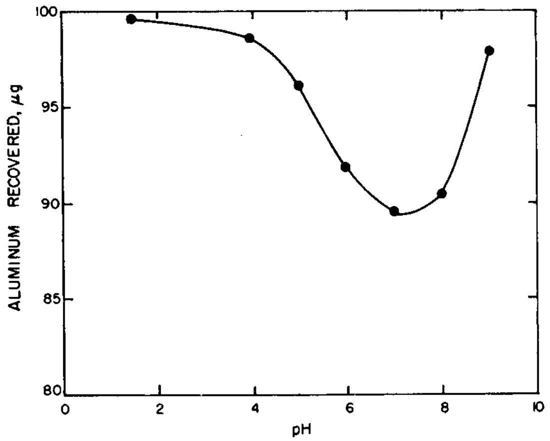

Fig. 1. Recovery of aluminium as the quinolate after removal of interferences by extraction with sodium diethyldithiocarbamate and chloroform at different pH values aluminium, μg, 100

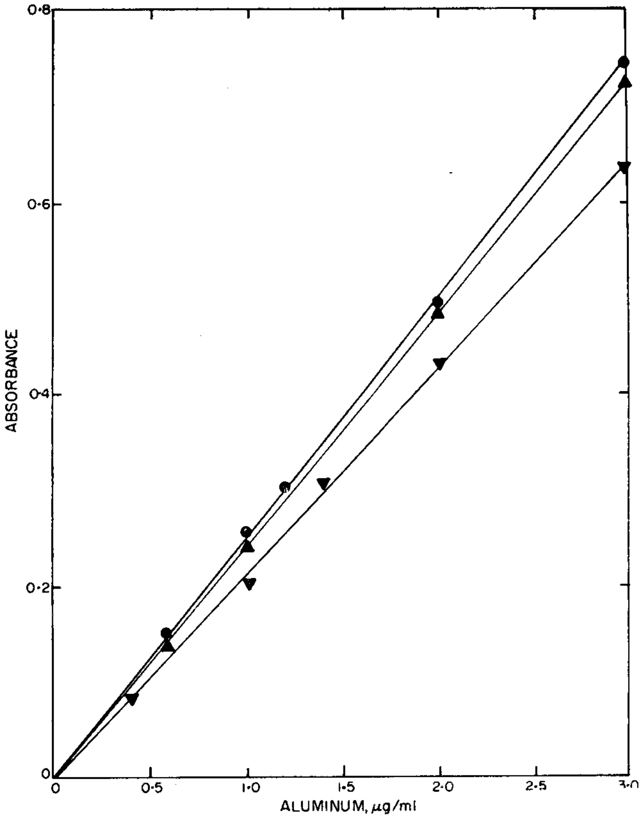

Fig. 2. Calibration curves for aluminium

● 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, Natriumcyanid 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-diäthyldithio-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 0.2N 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 1N 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 0·2N sulphuric acid or 0.8N 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 4M 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).

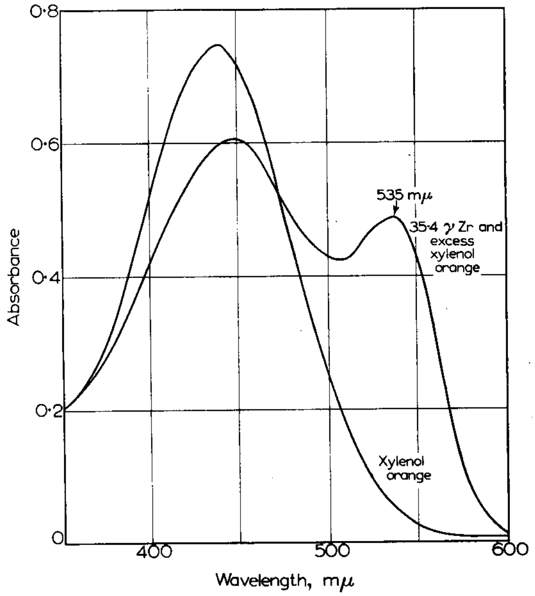

FIG. 1

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

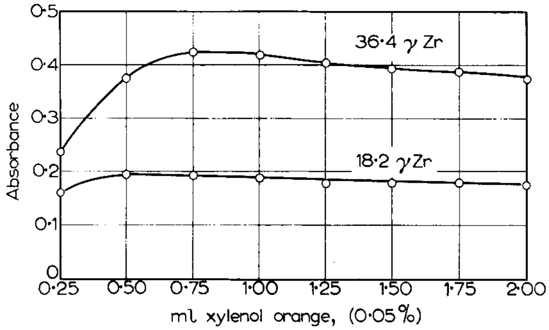

FIG. 2

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.

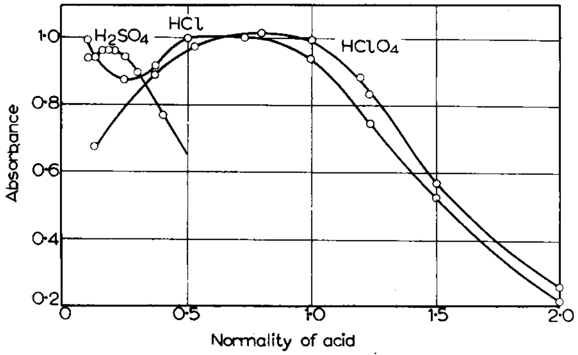

FIG. 3

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 0.01*M* metal solution to be tested, two drops of 0.25*N* 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 (0.5*N*) 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 0.5*N* 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 1*M* 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 0.1*M*	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 0.8*N* 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 0.5*N* 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 *mm ole*	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 0,2*N* 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_{In}/K_{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—$[GaCl_4]^{-}$–, das Indium als Tetrajodoindat-Ion—$[InJ_4]^{-6}$ 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.

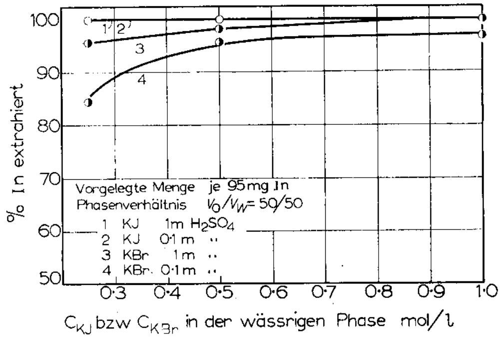

ABB. 1. Extrahierbarkeit von Indium mit Cyclohexanon aus wässrigen Kaliumbromid- und Kaliumjodidlösungen.

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 $-\underset{\underset{\displaystyle O}{\|}}{C}-$ (Carbonsäureester, Ketone, Kohlensäureglykolester), $-\overset{|}{\underset{\underset{\displaystyle O}{\|}}{P}}-$ (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.

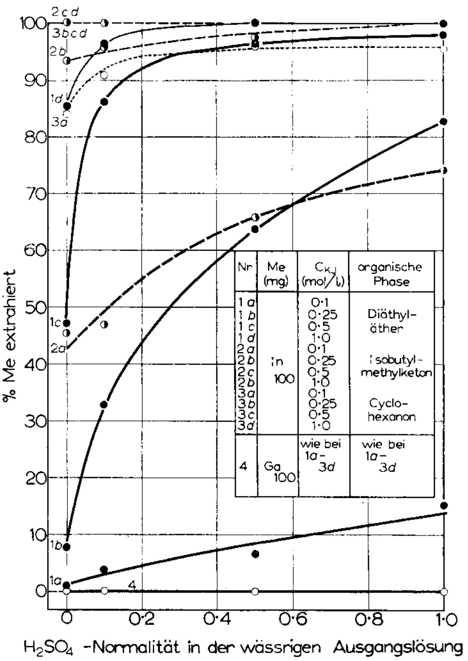

ABB. 2. Die Extrahierbarkeiten von Gallium und Indium in Abhängigkeit vom Schwefelsäuregehalt der wässrigen Ausgangslösung (Phasenverhältnis $V_0/V_w = 50$ ml/50 ml)

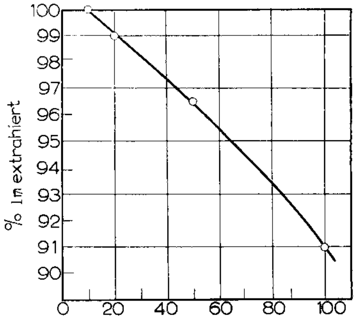

ABB. 3. Die Extrahierbarkeit von Indium mit Cyclohexanon aus 0,1 n schwefelsauren 0,1 m Kaliumjodidlösungen als Funktion der vorgelegten Indiummenge. (Phasenverhältnis $V_0/V_w = 50$ ml/50 ml).

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

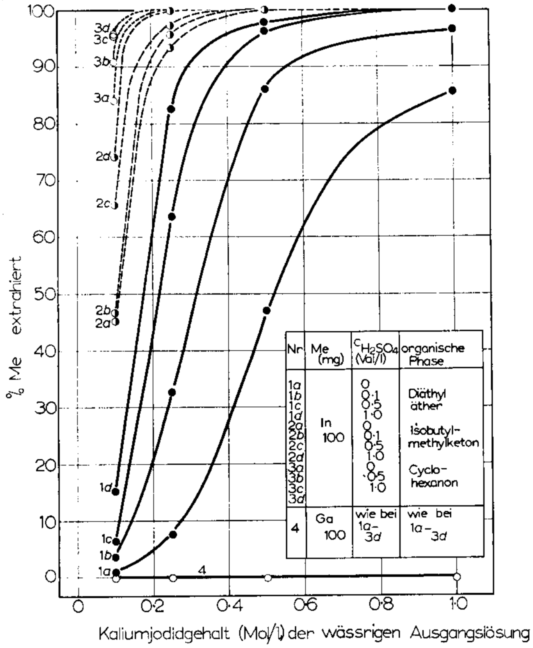

Abb. 4. Die Extrahierbarkeiten von Gallium und Indium in Abhängigkeit vom Kaliumjodidgehalt der wässrigen Ausgangslösung (Phasenverhältnis $V_0/V_w = 50$ ml/50 ml).

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
$C_{\mathrm{H_2SO_4}}$ (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.

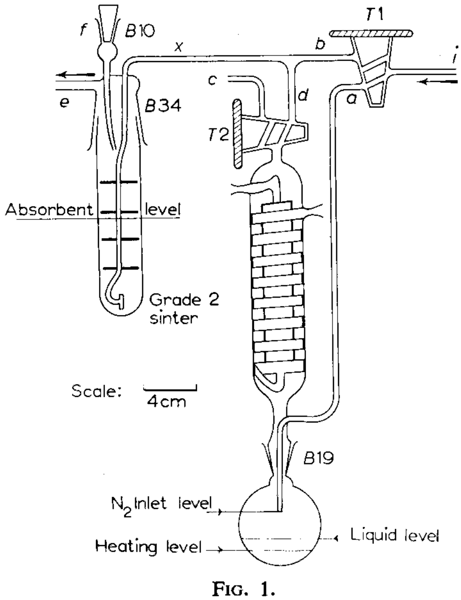

FIG. 1.

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 $Ba(OH)_2 \not> 0{\cdot}02$ ml 0·05*N*. (2) CO_2free distilled water, initially colourless to phenolphthalein, turned very faint pink. (3) alkalinity absorbed in HCl $\not> 0{\cdot}02$ 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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* Presented at a meeting of the Polarographic Society, held at Nobel Division, Imperial Chemical Industries Ltd., Stevenston, Ayrshire, on 26 September 1958.

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 $-1{\cdot}52$ 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 $0{\cdot}1\,M$ tetramethyl ammonium iodide base electrolyte, and a suitable maximum

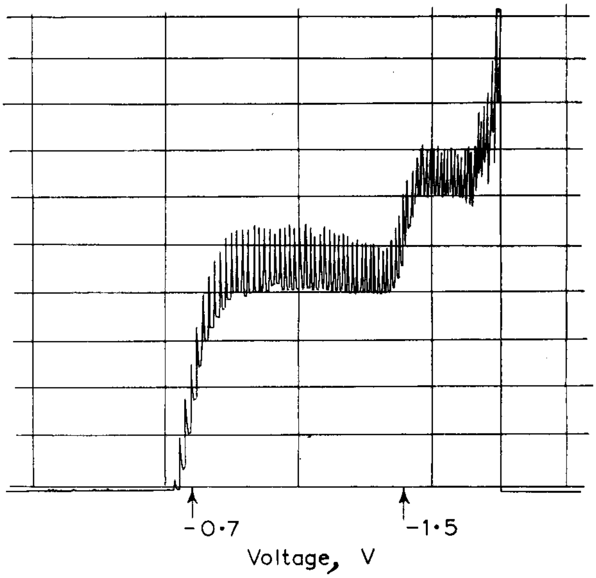

FIG. 1.—Polarogram obtained from dibutyl phthalate on Tinsley pen-recording polarograph in the presence of nitroglycerine.

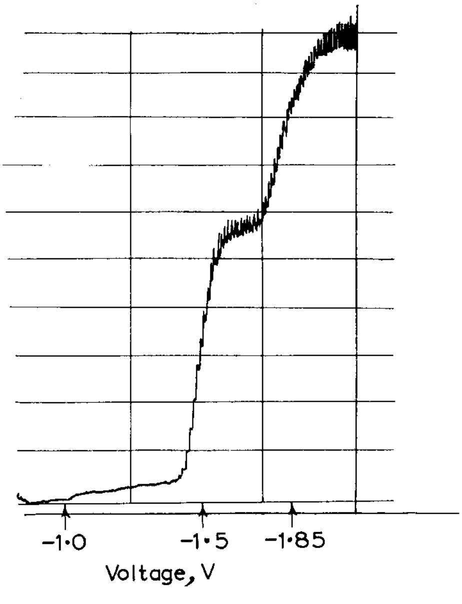

FIG. 2.—Polarogram obtained from dibutyl phthalate on Tinsley pen-recording polarograph, direct reading.

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 0·2M 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.

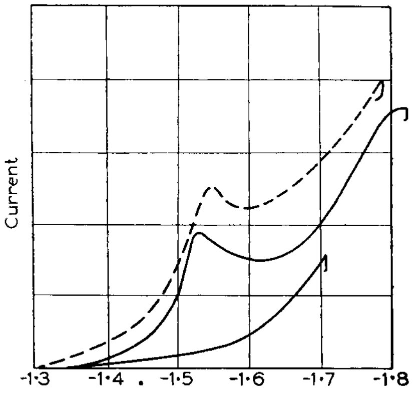

FIG. 3.—Polarogram obtained from dibutyl phthalate on cathode-ray polarograph. The broken line shows the effect of nitroglycerine on the dibutyl phthalate trace. The lower line shows the trace due to the nitroglycerine "blank" solution.

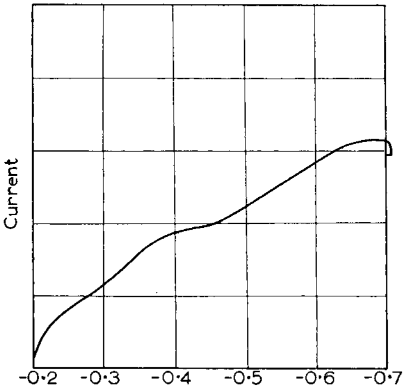

FIG. 4.—Polarogram obtained from nitroglycerine on cathode-ray polarograph.

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.

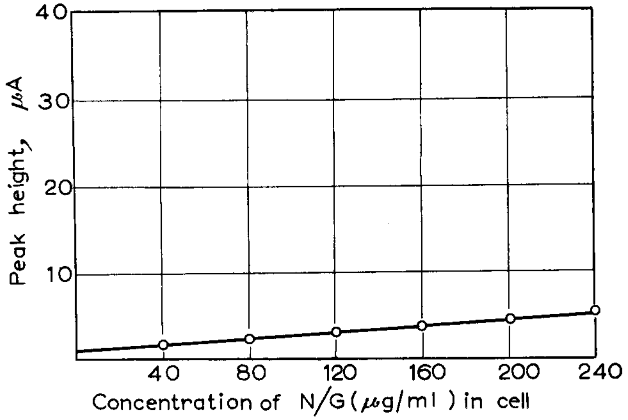

FIG. 5.—Polarographic behaviour of nitroglycerine in the method for dibutyl phthalate.

(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.

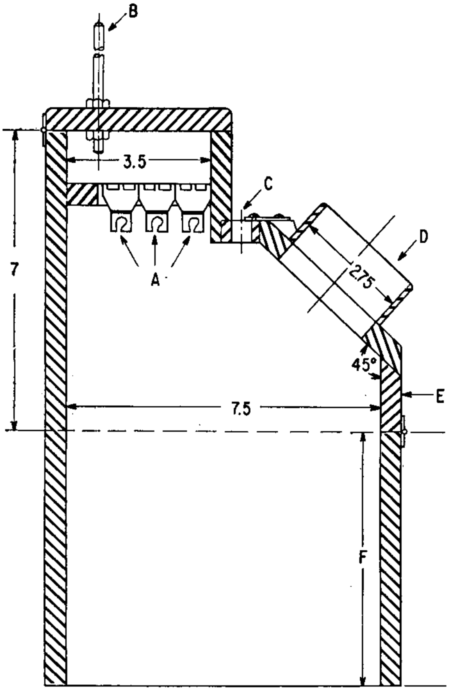

FIG. 1. Section through apparatus for fluorescent titrations.
(The arrows, A, indicate the lamp sockets, since the lamps are in the direction perpendicular to the plane of the paper.)

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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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.

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)	$1·12_5$ $1·12_5$	$135·4_8$ $132·4_5$	$134·1_4$ $131·1_1$	$133·6_5$ $130·6_2$
Filter paper disc + AgI precipitate	$1·12_5$	131·22	$142·9_0$ (disc + ppt.)	$141·3_2$ (disc + ppt.)
Millipore filter disc (H.A. assay type)	1·00	$15·1_7$	$15·1_5$	$15·1_4$
Millipore filter disc + AgI precipitate	$1·12_5$	25·10	$49·5_8$ (disc + ppt.)	$49·5_5$ (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.

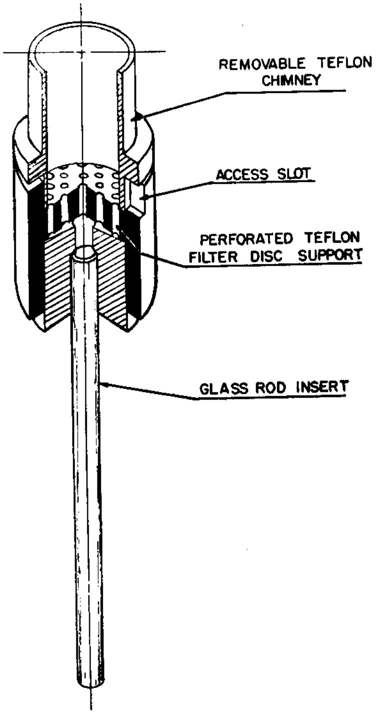

FIG. 1. Filtration assembly

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

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 $m\mu l$ of the test solution with about 50 $m\mu l$ of potassium ethyl xanthate solution (sat. aq.) Add about 50 $m\mu l$ of $2N$ HNO_3 or $2N$ HCl. An immediate pink to purple coloration (the shade depending on the concentration of technetium) is produced. Centrifuge. Add approximately 40 $m\mu l$ 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 $10N$ 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 $m\mu l$ of the dimethylglyoxime reagent to a cone containing about 100 $m\mu l$ of the test solution. Then add about 50 $m\mu l$ 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 $2N$ 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 $m\mu l$ of the test solution add 50 $m\mu l$ of $2N$ 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 $6N$ 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 $m\mu l$ of the test solution add 50 $m\mu l$ of $6N$ hydrochloric acid followed by 40 $m\mu l$ 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 $10N$ 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] (0·12*M* 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 (10*N*), 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 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).

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, 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.

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.

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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 Symposiumon** *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$^{\mathrm{III}}$ 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).

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirement

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, research papers should follow the pattern: *Introduction*, *Discussion*, *Conclusion*, *Experimental* (or such of these headings as apply).

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

4. Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, since they are easily available to the printers:

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5. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, *e.g.*, standard deviation. The same information should not be reproduced in both tables and figures.

6. References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

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

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

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CONTENTS

Short Communications:

Preliminary Communications:

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