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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 28, No. 1, January 1963

A SCHEME FOR THE ANALYSIS OF MONAZITE AND MONAZITE CONCENTRATES

A scheme using ion-exchange methods is described for the analysis of monazites and monazite concentrates. The sample is opened up with concentrated sulphuric acid, and the resultant solution is applied to a column of Zeocarb 225 resin. After phosphate has been washed out, lead, aluminium, titanium, iron, uranium, calcium and magnesium are eluted with *N* hydrochloric acid and determined by specific, mainly spectrophotometric, methods. Rare earth elements are eluted with 3 *N* hydrochloric acid. Cerium is separated from the other rare earths by solvent extraction of its nitrate with methyl iso-butyl ketone; both groups are determined gravimetrically. Thorium is eluted from the ion-exchange resin with 3.6 *N* sulphuric acid and determined spectrophotometrically with thorin.

The sulphuric acid-insoluble minerals are brought into solution by a double fusion method, and the determinations are carried out by a combination of ion-exchange and photometric procedures.

Silica, phosphorus pentoxide, tin and chromium are determined by photometric methods, using separate portions of the sample.

Lanthanum, yttrium and ytterbium are determined in a 1 *M* perchloric acid solution of the mixed rare earth oxides (less cerium) using flame photometry. Samarium, praseodymium and neodymium are determined by spectrophotometry.

K. S. CHUNG AND J. P. RILEY, *Anal. Chim. Acta*, 28 (1963) 1–29

DETERMINATION OF TRACES OF VITAMIN B_{12}

(in French)

An indirect determination of traces of vitamin B_{12} is proposed; the vitamin is decomposed and the liberated cobalt is determined colorimetrically with Nitroso-R salt. 5–10 μg of B_{12} can be determined. The use of tracers and internal standards decreases the error to less than 6%. Before the decomposition of the B_{12} all traces of ionic cobalt are removed by means of an ion-exchange resin. The method is very sensitive and fairly selective; only homologues of B_{12} containing cobalt interfere. B_{12} can be determined in many pharmaceutical products.

D. MONNIER, Y. GHALIOUNGHI AND R. SABA, *Anal. Chim. Acta*, 28 (1963) 30–40

DETERMINATION OF ZIRCONIUM AND HAFNIUM WITH XYLENOL ORANGE AND METHYLTHYMOL BLUE

Both Xylenol Orange and Methylthymol Blue are highly selective and sensitive reagents for zirconium and hafnium forming intensely red complexes in an acidic medium. The factors affecting the color formation have been studied. The properties of the complexes have been determined and compared. In general, zirconium forms a more stable complex with the two dyes than hafnium, and Xylenol Orange forms a stronger complex with either zirconium or hafnium than Methylthymol Blue. Hydrogen peroxide can completely mask the zirconium complexes of either dye but only slightly affects the hafnium complex of Xylenol Orange. Zirconium and hafnium can both be determined without separation using peroxide as a masking agent and sulfate as a demasking agent. A bleaching reaction was observed when small amounts of hafnium were added to the red zirconium complex of Methylthymol Blue in 2.4 *N* perchloric acid or a small amount of zirconium was added to the red hafnium complex of Methylthymol Blue solution at pH 2 to 3.

K. L. CHENG, *Anal. Chim. Acta*, 28 (1963) 41–53

DETERMINATION OF CADMIUM IN URANIUM BY ION EXCHANGE AND SQUARE-WAVE POLAROGRAPHY

Traces of cadmium in uranium and its compounds can be determined by ion-exchange separation and square-wave polarography. With a small column of anion-exchange resin, cadmium can be separated from uranium and recovered quantitatively from hydrochloric acid solution. Separations of cadmium from uranium are not perfect but are sufficient for the determination of traces of cadmium by square-wave polarography. The lower limit of the method is 0.01 p.p.m. of cadmium.

F. NAKASHIMA, *Anal. Chim. Acta*, 28 (1963) 54–60

COLOUR REACTION OF SCANDIUM WITH QUERCETIN AND ITS APPLICATION TO THE ANALYSIS OF SCANDIUM

A spectrophotometric study of the scandium–quercetin complex is described; μg amounts of scandium can be determined with quercetin at 435 mμ and pH 4.4. A 1 : 1 complex is formed. The apparent instability constant of the complex was estimated as $2.7 \cdot 10^{-7}$ by a spectrophotometric method. An ion-exchange method for separating scandium from several interfering ions is described.

H. HAMAGUCHI, R. KURODA, R. SUGISITA, N. ONUMA AND T. SHIMIZU, *Anal. Chim. Acta*, 28 (1963) 61–67

THE WET CHEMICAL ANALYSIS OF CERTAIN IMPURITIES IN HIGH-PURITY BERYLLIUM

Photometric methods for the analysis of iron, nickel, copper, aluminum, silicon, chromium and manganese in high-purity beryllium are described.

E. N. POLLOCK AND L. P. ZOPATTI, *Anal. Chim. Acta*, 28 (1963) 68–77

A COMPLEXIMETRIC METHOD FOR THE DETERMINATION OF DISSOLVED OXYGEN IN WATER

A new method is proposed for the determination of dissolved oxygen in water. The iron(III) formed from FES at pH 7.5 is titrated with EDTA solution in presence of salicylic acid indicator after adjustment of the pH to about 2.4 The method is slightly less precise than the WINKLER method for pure waters but more accurate for polluted waters; it is simple and convenient for field use.

R. TH. ROSKAM AND D. DE LANGEN, *Anal. Chim. Acta*, 28 (1963) 78–81

MICROHETEROMETRIC TITRATIONS OF LARGE ORGANIC NITROGEN-CONTAINING COMPOUNDS AND OF HETEROPOLY ACIDS

Micro amounts of nitron, quinine, strychnine, papaverine, yohimbine, nicotine, atropine, morphine or phenanthroline were titrated heterometrically with silicotungstic, phosphotungstic or phosphomolybdic acids at pH 1 or 7. The heterometric curves and the compounds obtained were studied. The reverse titrations were also studied. Microheterometric determinations of large nitrogen-containing compounds and heteropoly acids are suggested.

M. BOBTELSKY AND I. BARZILY, *Anal. Chim. Acta*, 28 (1963) 82–90

THE INTERFERENCE OF THALLIUM IN THE SPECTROPHOTOMETRIC DETERMINATION OF ANTIMONY AS IODOANTIMONITE

(Short Communication)

M. J. MAURICE AND R. L. M. VAN LINGEN, *Anal. Chim. Acta*, 28 (1963) 91–92

NOTE CONCERNING THE POTENTIOMETRIC DETERMINATION OF VANADIUM IN STEELS

(Short Communication, in French)

G. ROLAND, *Anal. Chim. Acta*, 28 (1963) 93–96

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A SCHEME FOR THE ANALYSIS OF MONAZITE AND MONAZITE CONCENTRATES

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(Received July 25th, 1962)

The mineral monazite is probably quantitatively the most important ore of both thorium and the rare earth elements. Chemically the mineral is an orthophosphate of the rare earth elements, principally those of low atomic number. Thorium is usually present in amounts varying from nil to as much as 28.2% (as ThO_2)[1]. Small amounts of other elements, such as silicon, calcium, magnesium, iron, beryllium, aluminium, titanium, zirconium, uranium and lead are present, some occurring in the lattice, others existing in mineral inclusions such as zircon and rutile, which are sometimes present in the grains.

In nature, commercially valuable monazite deposits are only found in fluvial and beach placers, in which the mineral is associated with other heavy detrital minerals such as zircon, magnetite, garnets, rutile, ilmenite, chromite, tantalite and cassiterite. Monazite is separated from these other minerals by flotation and by gravitational and magnetic methods.

The analysis of monazite concentrates is therefore divided into two parts: (*1*) the examination of the monazite mineral itself, which is usually taken as the fraction made soluble by heating with concentrated sulphuric acid, (*2*) the examination of the other minerals (the fraction unattacked by sulphuric acid); this fraction generally contains silicon, calcium, magnesium, iron, aluminium, titanium, zirconium (+ hafnium) and occasionally tin, chromium, niobium and tantalum.

Although a number of methods[2-5] have been used for the determination of lead, thorium and uranium in monazites, usually for dating purposes, very little work appears to have been carried out on the development of a scheme for the analysis of the mineral and its concentrates. Gravimetric procedures for the analysis of monazites have been described by MINER[6], DE OLIVEIRA[7], WILLIAMS[8], and SCHOELLER AND POWELL[9]. A microchemical procedure, using only 100 mg of sample, has been published by HECHT AND KROUPA[10]. In all these schemes, the separation of the rare earth group, cerium and thorium from one another and from other elements present, is made by precipitation. Such separations tend to be very time-consuming, since, owing to co-precipitation, it is nearly always necessary to purify the precipitate by dissolving and reprecipitating. This is likely to lead to loss of material, either mechanically or owing to the appreciable solubility of many of the precipitates, particularly the rare earth oxalates[11].

Although ion-exchange separations are generally cleaner and more satisfactory than

those achieved by precipitation, they do not appear to have been used for the analytical separation of the rare earth elements from the other elements occurring in monazite. Their use for the separation of the rare earth elements from one another is, of course, well established. Since the work described in this paper was completed, EDGE AND AHRENS[12] have described an ion exchange–spectrochemical method for the concentration and determination of traces of scandium, yttrium, neodymium, cerium and lanthanum in silicate rocks. In this procedure non-rare earth elements were eluted from a column of Dowex 50 using 3 *N* hydrochloric acid, and the rare earth elements were then eluted with 6 *N* hydrochloric acid. Anion-exchange methods have been employed for the adsorption of the sulphato-thorium anion in the determination of thorium in monazites[13,14]. A cation-exchange process has been employed for the determination of thorium in low grade ores[15].

This paper describes a scheme for the analysis of monazite concentrates, in which the principal cations present are divided into groups using ion exchange and solvent extraction. Each of these groups is analysed by selective methods. Silica, phosphorus pentoxide, chromium oxide and tin oxide are determined in separate portions of the sample using spectrophotometric procedures.

Opening up of monazite

Of the methods which have been used for the decomposition of monazite, that employing digestion with concentrated sulphuric acid is the most selective, and leaves most of the associated minerals practically unattacked. This method was therefore employed for opening up the monazite to give a solution which could be directly applied to a cation-exchange column. The resistant minerals, which remain after the sulphuric acid digestion, are brought into solution by a sodium carbonate fusion, followed by an evaporation with hydrofluoric acid to remove silica. This is followed by a bisulphate fusion to bring oxide minerals into solution. Cassiterite and chromite are only partially dissolved by this opening-up process. Phosphorus pentoxide is determined spectrophotometrically on the sulphuric acid digest of monazite.

A sodium hydroxide fusion is used to decompose the sample for the determination of silica. This has the advantage that the rare earths, zirconium, and thorium, remain as an insoluble precipitate and do not interfere in the subsequent photometric determinations.

Development of ion-exchange method for analysis of sulphuric acid digest

Tests were carried out to determine the most satisfactory eluants for the separation of the rare earth group, thorium and other elements likely to be present in the sulphuric acid digest. A column (46 cm long by 1.3 cm diameter) of Zeocarb 225, which is a sulphonated polystyrene 8% cross-linked with divinylbenzene, was used as adsorbent. Known amounts of these cations were adsorbed onto the resin column from 200 ml of a solution 0.2 *N* in sulphuric acid, containing 0.9 g of 85% orthophosphoric acid.

In order to remove phosphoric acid, which interferes with many of the determinations, the column was washed until the eluate gave no reaction for phosphate; this required 2 l of water. Phosphoric acid is strongly adsorbed by cation-exchange resins. SAMUELSON[16] has stated that it is more readily removed by washing with 0.01 *N*

TABLE I

ELUTION OF CATIONS FROM ZEOCARB 225 COLUMN WITH 8 × 250 ml PORTIONS OF *N* HCl

Element	*Oxide taken (mg)*	*Wt. (mg) of element (as oxide) in eluate*									*% Recovery*
		1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*Total*	
Calcium	25.0	0.00	0.00	0.00	4.48	15.68	4.41	0.35	0.00	24.92	99.6
Magnesium	25.0	0.00	18.59	6.36	0.10	0.00	0.00	0.00	0.00	25.05	100.2
Manganese	5.0	2.47	2.54	0.01	0.00	0.00	0.00	0.00	0.00	5.02	100.4
Lead	20.0	18.93	1.02	0.00	0.00	0.00	0.00	0.00	0.00	19.95	99.8
Aluminium	15.0	0.00	0.00	0.00	1.30	12.40	1.40	0.10	0.00	15.20	101.3
Iron	17.21	0.289	7.06	9.10	0.62	0.13	0.01	0.00	0.00	17.21	99.9
Tin	107.6	105.6	2.4	0.00	0.00	0.00	0.00	0.00	0.00	108.0	100.4
Uranium	20.0	19.60	0.50	0.00	0.00	0.00	0.00	0.00	0.00	20.1	100.5
Titanium	8.0	←			7.96		→	0.00	0.00	7.96	99.5
Sodium	50.0	←	49.5	→	0.50	0.00	0.00	0.00	0.00	50.0	100.0
Potassium	20.0	←	20.0	→	0.00	0.00	0.00	0.00	0.00	20.0	100.0
Ytterbium	324.3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
Praseodymium	298.9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
Yttrium	342.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0
Thorium	100.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0

hydrochloric acid than with water, but this did not prove to be the case with Zeocarb 225, and even 0.1 *N* hydrochloric acid was no more effective than water.

Each column was then eluted with 8 × 250 ml aliquots of *N* hydrochloric acid, and each eluate was analysed. The results, which are shown in Table I, indicate that 2 l of *N* hydrochloric acid completely eluted calcium, magnesium, manganese, lead, aluminium, iron, tin, titanium, uranium, sodium and potassium.

The rare earth group and thorium were not eluted with this strength of hydrochloric acid. The elution of the columns containing these elements was continued with 6 × 250 ml aliquots of 2 *N* hydrochloric acid. It was found that although yttrium and the rare earths of higher atomic number, such as ytterbium, were eluted with 750 ml of the 2 *N* hydrochloric acid, those of low atomic number were not completely removed with 1500 ml. The experiment was therefore repeated and the final elution was carried out using 6 × 100 ml aliquots of 3 *N* hydrochloric acid. In this case, the elution of the rare earth elements was complete after 500 ml had passed through the column (Table II).

TABLE II

ELUTION OF RARE EARTHS AND THORIUM WITH 3 *N* HCl

Element	*% Recovery 100 ml portions of 3 N HCl*						
	1	*2*	*3*	*4*	*5*	*6*	*Total*
Ytterbium	93.4	6.4	0.1	0.0	0.0	0.0	99.9
Praseodymium	34.9	50.3	12.8	1.7	0.3	0.0	100.0
Yttrium	87.1	12.0	0.9	0.0	0.0	0.0	100.0
Thorium	0.0	0.0	0.0	0.0	0.0	0.1	0.1

It appears that there is a very marked difference in retentivity between the two sulphonated cross-linked polystyrene resins Zeocarb 225 and Dowex 50. EDGE AND AHRENS[12] required 330 ml of 3 *N* hydrochloric acid to remove the common cations from a similar column of Dowex 50 and used 700 ml of 6 *N* hydrochloric acid to elute the rare earth elements.

Thorium was not appreciably eluted even with 600 ml of 3 *N* hydrochloric acid. The quantitative removal of thorium from the resin was a matter of considerable difficulty. If the elution was carried out with 4 *N* nitric or hydrochloric acid, thorium was gradually removed, but several litres of acid would have been required to remove it quantitatively. Elution with 500 ml of 6 *N* nitric acid gave a 97.5% recovery, but its use was not further investigated as the resin was oxidised by this strength of acid, particularly if the room temperature rose above 20°.

KAPATSINSKAYA AND SYROMYATNIKOV[17] have used a 5% solution of oxalic acid for the elution of thorium adsorbed on Kationit KU2 resin. The use of this eluant was therefore investigated and it was found that although 0.5 *M* oxalic acid undoubtedly rapidly removed thorium from the Zeocarb 225 columns, it was impossible to achieve a recovery greater than 92%. The reason for this poor recovery could not be determined, but in a considerable number of tests recoveries of 83–87% were generally obtained. Elution with 5% citric acid at pH values of from 4.0–6.1 was also attempted, and recoveries of about 83–90% were obtained using 175 ml. Although it is probable that better recoveries could be achieved using larger volumes of citrate,

the investigation was not continued owing to the extreme difficulty of destroying the eluant and obtaining colourless solutions for spectrophotometry.

Since thorium forms a stable sulphato-thorium anion, it was thought that sulphuric acid might be a suitable agent for eluting the element from the cation-exchange resin. This proved to be the case, and it was found that 600 ml of 3.6 *N* sulphuric acid eluted 99.7% of the thorium from the column, and a further 200 ml of the acid only removed 0.26%.

The final conditions selected for the elution of the cations from the sulphuric acid digests of the monazites were as follows:

(*1*) 1970 ml of 1 *N* hydrochloric acid.
(*2*) 750 ml of 3 *N* hydrochloric acid.
(*3*) 800 ml of 3.6 *N* sulphuric acid.

These eluates were then analysed as described below.

Analysis of N hydrochloric acid eluate

Before analysis 1 l of this eluate is evaporated to fuming with perchloric acid and diluted to 100 ml. The following elements are determined in this solution (solution B): aluminium, calcium, magnesium, iron, lead, titanium and uranium. In addition, manganese and the alkali metals, which are only rarely found in appreciable amounts in the acid-soluble fractions of monazites can also be determined in this eluate.

Determination of aluminium

Aluminium is determined spectrophotometrically in solution B by extraction of its 8-hydroxyquinoline complex[18]. Uranium, which interferes in this method, is removed by adsorption of its acetate complex, on a column of the anion-exchanger Amberlite IRA 400, in its acetate form[19]. Interference of iron is prevented by complexing it as the ferrous tris-dipyridyl complex. Of the other elements present in the 1 *N* hydrochloric acid eluate, only titanium interferes slightly, but compensation can be made for its interference.

Determination of calcium and magnesium

Calcium and magnesium are determined in solution B by photometric titration with ethylenediaminetetraacetic acid as described by RILEY AND WILLIAMS[20]. Interfering elements, such as lead, iron, aluminium, titanium and uranium, are removed by prior solvent extraction of their 8-hydroxyquinoline complexes[21].

Determination of iron

The determination of iron in solution B is carried out photometrically using 2,2′-dipyridyl. This method is known to be free of interference from other cations.

Determination of lead

Although both normal[22] and square-wave[2] polarography have been used for the determination of lead in monazite, it was thought that greater precision could be attained by means of a spectrophotometric procedure.

Few colorimetric reagents are available for the determination of trace amounts of lead. Of these, dithizone is the most widely used on account of its high sensitivity which allows even submicrogram amounts of lead to be determined. It is, however,

subject to interference by a number of other elements, which form coloured dithizonates extractable by carbon tetrachloride in the pH range (8–11) used for extraction of lead dithizonate. Their interference can, however, be much reduced by suitable masking agents, such as citrate and cyanide.

A further source of error in the determination of lead is caused by phosphate if considerable amounts of rare earth elements or thorium are also present, since the phosphates of these elements are only slightly soluble in ammonium citrate and co-precipitate lead strongly. By working at pH 9.2 in order to minimise this precipitation, POWELL AND KINSER[23] have used dithizone for the direct determination of lead in the sulphuric acid digests of monazites. But even at this pH they seem to have encountered occasional low recoveries. In the present method, phosphate, rare earth elements and thorium are removed by the preliminary ion-exchange separation and this difficulty does not arise.

In many of the methods described in the literature for the determination of lead, a preliminary extraction with concentrated dithizone solution is carried out, both to concentrate lead and to separate it partially from interfering elements. The concentration of lead in the 1 *N* hydrochloric acid eluate from monazite is relatively high compared with the concentrations of possible interfering elements. It was therefore decided to omit the preliminary extraction stage and to extract lead from the original hydrochloric acid eluate (solution A), with 0.001% dithizone in carbon tetrachloride after adjusting to pH 9.5 with ammonia and adding cyanide and citrate.

Under the conditions for the extraction and photometric measurement described on p. 18, it was found that BEER's law was obeyed up to 12.5 μg of lead, but with greater amounts, the optical density was less than expected; this was probably due to partial precipitation of lead dithizonate, for its solubility in carbon tetrachloride is only equivalent to 12 μg Pb/10 ml[24]. The method showed a coefficient of variation of 1% with 10 μg of lead (as PbO). The interference of a number of cations was investigated by extracting 15 ml aliquots of solutions of the cations both with and without the addition of 10 μg of lead. No interference was experienced with 1 mg of aluminium, antimony, calcium, gadolinium, nickel, magnesium, thorium, titanium or yttrium, or with 0.5 mg of cobalt, copper, iron, tin or uranium. Cadmium interferes slightly at the 1 mg level, but its interference would be negligible even if its concentration was ten times that of lead.

Determination of titanium

Titanium was determined in solution B using the hydrogen peroxide procedure described by RILEY[18]. Interference of iron is prevented with phosphoric acid. Uranium causes very slight interference, but this can be compensated for.

Determination of uranium

Although several polarographic[25], volumetric[26,27], gravimetric[28] and fluorimetric[29] procedures have been described for the determination of uranium in monazite, it seemed that for the present purpose a photometric method would be most suitable. MURPHY *et al.*[30] have determined uranium in monazite by extracting it as thiocyanate with tributyl phosphate and measuring the intensity of the colour of the yellow thiocyanate. This method is insensitive and subject to several interferences. Most of

the other colorimetric reagents which have been described for the colorimetric determination of uranium are unspecific, and of poor sensitivity.

BLANQUET[31] has used dibenzoyl methane[32] as a sensitive reagent for the determination of uranium in minerals. In his procedure the yellow complex was formed in an aqueous pyridine medium in the presence of EDTA and tartaric acid. A number of elements, particularly iron, and to a lesser extent thorium, interfere and were removed by carbonate precipitation. When this method was tested, it was found that the photometric procedure gave very satisfactory results, but that the removal of iron by carbonate precipitation led to coprecipitation of uranium. In a series of experiments where 4 mg of iron was precipitated from a solution containing 40 μg of uranium, the recovery of uranium averaged only *ca.* 70% (in contrast to the work of ERLENMEYER *et al.*[33] in which recoveries of better than 90% were claimed). For this reason, the carbonate precipitation method was not investigated further.

The uranyl ion can be extracted, probably mainly as the normal nitrate, from solutions of high nitrate concentrations by a variety of oxygen-containing organic compounds, such as ethers, esters, ketones and organic phosphates. The most frequently used technique[34,35] is to extract uranium with 10 ml of ethyl acetate from a solution containing *ca.* 10 g of aluminium nitrate in 10 ml of solution which is 0.5–1.0 *N* in nitric acid. According to ADAMS AND MAECK[35], recoveries of 90–95% can be obtained at a uranium level of 1 p.p.m. In the absence of chloride *ca.* 0.025% of the iron (0.2 g), and about 60% of thorium (2.5 mg) are extracted from the aqueous phase. These conditions would therefore give satisfactory separation of uranium from iron in solution B in the monazite analysis. The fact that thorium, which interferes in the colorimetric determination, is also extracted is not of importance since it is not eluted by 1 *N* hydrochloric acid. Trial experiments, in which uranium (50 μg as U_3O_8) was extracted by a double extraction with ethyl acetate, and determined using dibenzoyl methane as described below (p. 19), gave uranium recoveries of 93.3, 94.3 and 93.7%. Determinations carried out in the presence of 2 mg of ferric iron and of similar amounts of the other cations likely to be present in solution B, showed that possible interference from these ions had been eliminated by the extraction step. A linear calibration graph was obtained for the combined procedure in the range 0–250 μg U_3O_8.

Determination of manganese

The concentration of manganese in monazite occasionally reaches 0.1% but is generally much less. If desired, it can be determined in solution B by the method of NYDAHL[36], in which manganese is oxidised by persulphate in presence of silver catalyst, phosphoric acid being added to prevent interference by iron.

Determination of sodium and potassium

Sodium and potassium are occasionally present in small amounts in the sulphuric acid digests of monazite concentrates, and are presumably derived from acid attack on minerals such as felspars. They may be determined in solution B by flame photometry, after removal of interfering elements by ion exchange[18].

Determination of cerium and total other rare earths in 3 N hydrochloric acid eluate

The elution of the ion-exchange column with 3 *N* hydrochloric acid removes the rare

earth elements, of which cerium is the most abundant member, normally amounting to *ca.* 45% of the total rare earth elements. It is necessary to separate the cerium before the spectrophotometric or flame photometric determination of the other rare earth elements because it interferes.

Most analytical methods of separating cerium make use of the facts that it is the only rare earth which can be oxidised to the tetravalent state, and that the properties of cerium(IV) compounds are different from those of the trivalent rare earths. One of the most commonly used processes is based on the fact that cerium(IV) compounds are easily hydrolysed to insoluble ceric hydroxide at pH 3. Bromate[37] and permanganate[38] have been used for the oxidation, and in both of these methods oxidation and hydrolysis occur simultaneously. Both of these processes give only semiquantitative recoveries of cerium (*ca.* 97.6%[39]) and in the permanganate process, the recovered cerium may be only 98.5% pure. Cerium may also be precipitated as insoluble ceric iodate[40,41]. Both of these chemical separation methods suffer severely from the effects of coprecipitation of other rare earth elements, and it is always necessary to purify the cerium precipitate by reprecipitation.

Since solvent extraction techniques are free from the troubles such as coprecipitation which beset precipitation methods, it was decided to investigate their use for the separation of cerium. Tetravalent cerium is extractable from a nitric acid medium by a number of oxygen-containing organic solvents. Its extraction with diethyl ether at various nitric acid concentrations has been investigated by BOCK AND BOCK[42], who found that with equal volumes of the two phases 95.7% cerium was extracted from 6 *N* nitric acid. This procedure has been used by WYLIE[43] for the analytical separation of cerium from the other rare earths. Under the same conditions, about 0.3% of lanthanum is extracted. It is important that the ether should be free from peroxide since this can cause reduction of the cerium. The extraction must be carried out in subdued light to avoid photochemical reactions leading to the reduction of cerium(IV). WARF[44] has used tributyl phosphate for the extraction of cerium from 10 *N* nitric acid, but appreciable amounts of lanthanum and the lighter rare earths are also extracted.

GLENDENIN *et al.*[45] have studied the extraction of cerium with methyl iso-butyl ketone, and have found cerium to be satisfactorily extracted from 8–9 *N* nitric acid. This solvent has a number of advantages over diethyl ether for the extraction of cerium, since it does not peroxidise, it is much less volatile and does not creep like ether. The extraction of cerium and a number of rare earth elements with this solvent was therefore investigated.

The optimum nitric acid concentration for extraction of cerium by methyl isobutyl ketone was evaluated. Aliquots (50 ml) of solutions of cerium(III) (200 mg Ce) in appropriate strengths of nitric acid, were treated with 0.3 g of sodium bromate.

TABLE III

PERCENTAGE EXTRACTION OF Ce^{4+} WITH METHYL ISO-BUTYL KETONE AT 20°

Nitric acid normality	4	5	6	7	8	9	10[a]	11[a]
% Extraction	4.9	17.3	50.2	73.5	85.3	86.2	88.5	67.9

[a] Nitric acid reacted with solvent.

They were extracted for 5 min with 50 ml aliquots of methyl iso-butyl ketone, which had been previously equilibrated with the same strength of nitric acid. The organic phases were then analysed for cerium. The results (Table III) show that the optimum nitric acid concentration for the extraction is 9.5–10 *N*. Since this strength of nitric acid tends to react with the ketone, an acidity of 8.5 *N* was used in all subsequent work; under these conditions three extractions should extract *ca.* 99.8% of the cerium.

The extraction of lanthanum, ytterbium and yttrium from 8.5 *N* nitric acid by the ketone was investigated. It was found that the percentage extractions, using a single extraction, were 0.11, 0.14 and 0.13% respectively. It was concluded that the extraction of cerium should be carried out by extracting the 8.5 *N* nitric acid solution 5–6 times with the ketone. In order to prevent the extracted cerium being contaminated with rare earths, either by the small amount extracted by the ketone or by droplets from the nitric acid phase, the ketone phase should be washed once with 8.5 *N* nitric acid.

The efficiency of the separation process was tested by extracting mixtures of cerium and rare earths of known composition, as described on p. 20. The recovery of cerium and rare earths from the extraction was carried out by precipitation of the 8-hydroxyquinoline complexes and ignition to oxide. The results of these tests (Table IV) show that quantitative separation of cerium from the other rare earth elements has been attained.

TABLE IV

SEPARATION OF CERIUM FROM OTHER RARE EARTHS

	No added R_2O_3		*R = Yttrium*		*R = Ytterbium*		*R = Samarium*	
CeO_2 taken (g)	0.2248	0.2208	0.2122	0.2245	0.2202	0.2082	0.2499	0.2233
R_2O_3 taken (g)	—	—	0.2423	0.1915	0.2214	0.2214	0.1912	0.1984
CeO_2 found (g)	0.2253	0.2216	0.2124	0.2243	0.2205	0.2077	0.2515	0.2233
R_2O_3 found (g)	—	—	0.2421	0.1915	0.2216	0.2208	0.1909	0.1984

Determination of thorium in 3.6 N sulphuric acid eluate

Spectrographic[46,47], X-ray fluorescence[48,49], and radiochemical[50,52] methods have been employed for the direct determination of thorium in monazites. A number of organic acids, such as terephthalic and naphthionic acids have been applied to the separation and gravimetric determination of thorium in monazites[52–54]. All these reagents suffer from serious interference by sulphate, and before they could be applied to the analysis of the 3.6 *N* sulphuric acid eluate, would necessitate the evaporation of the eluate to dryness.

Several colorimetric methods are available for the determination of thorium and a number of these have been applied to its determination in monazites after separation from interfering elements by precipitation with oxalate[55–57] or iodate[58] or by solvent extraction[59,60].

A survey of the literature suggested that thorin (the disodium salt of 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid) is the most satisfactory reagent for the colorimetric determination of thorium. The optimum conditions for the formation of the red complex have been investigated by a number of workers. THOMASON *et al.*[61] have found that the optical density of the solution is constant in the pH range

0.2–1.0. CLINCH[62] recommends 0.5–1.5, whereas MAYER AND BRADSHAW[63] consider that this range is too large and recommend that the solution should be 0.3–0.4 *N* with respect to hydrochloric acid. Phosphate, oxalate, fluoride and much sulphate interfere seriously and must be removed. Zirconium forms an analogous complex, but its interference can be masked with *meso*-tartaric acid[60,64,65].

Since thorium is eluted from the Zeocarb 225 column using 3.6 *N* sulphuric acid, it is necessary to evaporate the sulphuric acid before carrying out the colorimetric determination; this is best achieved using an aliquot of the eluate. The residue from the evaporation is most conveniently dissolved in perchloric acid, because most of the other mineral acids complex thorium. The optimum conditions for the determination of thorium in the presence of perchloric acid using thorin were therefore investigated. It was found that an acidity of up to 3.0 *N* with respect to perchloric acid in the final solution had no effect on the colour of the complex, when measured against a reagent blank having the same acidity. This is in marked contrast to earlier methods using hydrochloric acid, in which erratic results are obtained unless the acidity is kept within close limits. A final concentration of 0.9 *M* (*i.e.* 2.5 ml of 60% perchloric acid per 25 ml) was used in all subsequent work. With 5 ml of 0.1% thorin, as described on p. 21, BEER'S law was obeyed up to at least 300 μg of ThO_2/25 ml. Replicate determinations carried out with 125 μg ThO_2 showed that the coefficient of variation of the method was 0.4%.

In general, interferences in the thorium method are few. No interference was given by the following ions: Pb^{2+} (20 mg), Al^{3+} (20 mg), Cu^{2+}, Ag^{+}, Be^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ga^{3+}, Ti^{4+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} (1 mg of each), Sc^{3+}, Gd^{3+}, In^{3+}, Ti^{+}, UO_2^{2+} (100 μg of each). Iron(III) interferes somewhat, but its interference can be completely prevented by reduction with hydroxyammonium chloride. Interferences by zirconium and titanium are more serious (0.25 mg Zr^{4+} = 28 μg Th, 25 mg Ti^{4+} = 31 μg Th), but since these elements are both eluted from the ion exchanger by *N* hydrochloric acid, they would be absent from the 3.6 *N* sulphuric acid eluate.

Analysis of sulphuric acid-insoluble minerals

The insoluble residue from the sulphuric acid digestion of monazites is generally of complex composition. It may contain a number of oxide minerals, such as rutile, quartz, magnetite and ilmenite, together with silicate minerals. The following elements are usually present: calcium, magnesium, aluminium, iron, titanium, zirconium and silicon. Occasionally niobium, tantalum, chromium and tin may also be found in the residue. In the proposed method, the resistant minerals are opened up by a sodium carbonate fusion, followed by an evaporation with hydrofluoric acid and then a bisulphate fusion. This process brings all the minerals normally associated with monazite into solution, with the exception of cassiterite and chromite, which are only partially attacked. Niobium and tantalum, if present, remain as their oxides after the bisulphate fusion, and may be determined by chromatography[66].

The determinations of iron and tantalum in the solution of the residue are carried out by the methods used for the analysis of solution B. Zirconium is determined spectrophotometrically with quinalizarinsulphonic acid[67] in the presence of hydroxyammonium chloride to prevent interference by iron. Titanium does not interfere.

Since zirconium seriously interferes in the spectrophotometric determination of aluminium with 8-hydroxyquinoline, it is separated from it by an ion-exchange

method. The cations in the solution are adsorbed on a short column of Zeocarb 225. Aluminium is eluted with 300 ml of 0.1 *M* lactic acid (which has been adjusted to pH 5.8 with ammonia), and is determined spectrophotometrically in the eluate after extraction with 8-hydroxyquinoline. Some iron is also eluted, but its interference in the photometric determination is prevented by complexing with dipyridyl; negligible amounts of titanium are also eluted. Zirconium, titanium, hafnium and most of the remaining iron are eluted with 80 ml of 0.05 *M* oxalic acid; this fraction can be used for the spectrographic determination of the zirconium to hafnium ratio if desired. The elution of calcium and magnesium is carried out with 45 ml of 3 *N* hydrochloric acid. These elements are determined by titration with EDTA after extraction to remove traces of iron.

Determination of phosphorus pentoxide

Phosphorus pentoxide is determined by a photometric molybdenum blue method[68] using an aliquot of a solution prepared by digestion of the monazite with concentrated sulphuric acid. It was found that no interference was experienced in the spectrophotometric method (p. 24) in the determination of 25 μg of phosphorus pentoxide in the presence of iron, aluminium, calcium, magnesium, zirconium, thorium, titanium, samarium or lead (200 μg of each) or of 30 μg of niobium or 50 μg of uranium. BEER's law is obeyed up to at least 90 μg of P_2O_5 (50 ml final volume) and replicate determinations carried out with 50 μg of P_2O_5 showed the coefficient of variation of the method to be 0.3%.

In order to check that all the phosphate was dissolved by the digestion procedure, the insoluble residues from two monazites were brought into solution and analysed for phosphorus. Concentrations of 1.2% and 1.3% of P_2O_5 were found, corresponding with 0.017% and 0.014% P_2O_5 in the total monazite, showing that retention of phosphate by the residue is negligible.

Determination of silica

The determination of silica is carried out on a separate portion of the monazite by a modification of the method described by RILEY[18]. The sample is fused with sodium hydroxide and the fused cake is dissolved in water. Silica is determined in the acidified solution by a molybdenum blue method. The formation of phosphomolybdenum blue is prevented by the addition of oxalic acid. The SiO_2 : P_2O_5 ratio in monazites (*ca.* 1 : 30) is very different from that in silicate rocks (> 300 : 1), for which the method was originally developed. Photometric determinations were therefore carried out on mixtures of silicate and phosphate in the ratio in which they occur in monazites. It was found that although these amounts of phosphate alone gave no colour with the reagent, in the presence of silica the expected intensity of the silicomolybdenum blue did not develop. This was attributed to competitive reactions between the silicate and phosphate for the moderate excess of molybdate present. Quantitative recoveries of silicate were obtained if smaller aliquots of the solution from the fusion were taken and the optical density was measured in 4 cm cells instead of the 1 cm cells normally used.

In order to determine whether all the silicate in monazite was rendered soluble by the alkali fusion, a fusion was carried out on a commercial sample of monazite. After leaching the cake and acidification as described on p. 24, the insoluble oxides were

recovered by centrifugation. They were fused again with sodium hydroxide and the silica was determined as before. It was found that the second fusion liberated silica equivalent to only 0.012% SiO_2 in the total monazite. A similar experiment carried out using zircon, which is the most resistant silicate likely to be found in monazite, also showed that silica is rendered almost completely soluble by the alkali fusion.

After the acidification of the liquid from the leaching of the cake from the alkali fusion, most of the rare earths, titanium, zirconium and thorium, remain as an insoluble residue. The acidic solution therefore contains only low concentrations of these elements. Tests were carried out to check whether these or other elements present in monazite would cause any interference in the photometric determination. It was found that no interference in the determination of 37.5 μg of silica was caused by 10 mg amounts of aluminium, iron, calcium, magnesium, lead, lanthanum, neodymium, uranium and thorium. Slight interference was caused by 3 mg of zirconium, but the concentration of zirconium likely to be found after a fusion is likely to be very low owing to the rapidity with which the zirconate ion hydrolyses.

Determination of tin

Cassiterite frequently occurs as a minor component of monazite concentrates particularly those of Australian origin. Since it is a very resistant mineral its occurrence is often indicated by the presence of dark insoluble grains remaining after solution of the bisulphate fusion. Tin is determined on a separate sample, by bringing cassiterite into solution by means of a sodium peroxide fusion. Tin is separated by distillation with hydrobromic acid[69] and determined photometrically. No interference is caused by any of the components of monazite concentrates.

Determination of chromium

Chromite is an occasional component of monazite concentrates, and its presence is indicated by the green colour of the cake from the bisulphate fusion used for opening up the residue. Chromium is determined by fusion of a separate portion of the sample with a mixture of sodium carbonate and sodium nitrate. After leaching with water, chromate is determined photometrically. The elements present in monazites do not interfere.

Determination of individual rare earth elements in mixed oxides (less cerium)

VICKERY[70] has reviewed the literature on the determination of rare earth elements by spectrophotometry and flame photometry. Although aqueous solutions of a few of the rare earths do not exhibit specific absorption in the ultraviolet, visible or near infrared regions of the spectrum, the majority show very complex absorption spectra consisting of many very sharp bands of low intensity. These bands overlap to such an extent as to make the determination of minor components of a rare earth mixture difficult, without previous separation of the mixture into simpler groups by ion exchange.

In the present work absorption spectrophotometry has been used only for the determination of neodymium, praseodymium and samarium in monazites. A 2% solution of the rare earth oxides, less cerium, is made in 1 *M* perchloric acid and the optical density of the solution is measured in 4 cm cells at 401.5, 444.2 and 521.9 mμ (the most suitable absorption maxima for samarium, praseodymium and neodymium

respectively). Since the absorption bands are extremely fine, the measurements are made at as narrow a bandwidth as possible. The $E_{1cm}^{1\%}$ values at these wavelengths, obtained with spectroscopically pure rare earth oxides, and measured with an Optika CF 4 spectrophotometer are given in Table V.

TABLE V

$E_{1cm}^{1\%}$ VALUES FOR DETERMINATION OF RARE EARTHS

Wavelength (mμ) *Bandwidth (Å)*	*401.5* *1.5*	*444.2* *0.8*	*521.9* *1.5*
Neodymium	0.0073	0.0079	0.264
Praseodymium	0.0019	0.603	0.0009
Samarium	0.1937	0.0107	0.0032

In using this table for calculating the rare earth composition, allowance must be made, by the use of simultaneous equations, for the effect of mutual interference. None of the other rare earth elements is present in monazites in sufficient amount to cause appreciable interference.

Next to cerium, lanthanum is the most abundant of the rare earths present in monazite. Since it has no absorption bands in the ultraviolet, visible or near infrared region of the spectrum, it is not possible to determine it spectrophotometrically. It does, however, have a flame spectrum which has a LaO band at 793 mμ, where there is no serious emission from any of the other rare earths. It was found that at this wavelength, using an oxy-acetylene flame, a linear relationship existed between emission intensity (% transmission) and lanthanum up to 0.2% La_2O_3, using a solution in 1 *M* perchloric acid. Under these conditions, with the flame photometer set to 100% transmission with 0.2% La_2O_3, 2% solutions of neodymium, praseodymium and samarium (the other principal rare earth elements in monazite) in 1 *M* perchloric acid, gave readings of 23.0, 19.2 and 13.2 respectively. Examination of mixtures of lanthanum with neodymium, praseodymium and samarium showed that, if allowance was made for the small amount of emission by these elements, satisfactory determinations of lanthanum could be made.

Monazite contains 2–8% of yttrium oxide in the mixed rare earth oxides; this element, like lanthanum, shows no characteristic absorption bands. Ytterbium, which is generally present in the mixed oxides from monazites to the extent of less than 0.5%, only possesses a very weak absorption band at 974 mμ, which is subject to interference by many other rare earth elements, notably erbium. These two elements can, however, be determined by flame photometry, using the oxy-hydrogen flame in place of the more usual oxy-acetylene flame, in order to reduce the background. With the wavelengths 613.2 mμ for yttrium and 398.9 mμ for ytterbium it was found that linear calibration graphs were obtained for solutions containing up to 0.2% Y_2O_3 and Yb_2O_3 in 1 *M* perchloric acid.

The effect of interfering elements was investigated. The flame spectrophotometer was set to 100% transmission with 0.2% solutions of the two oxides in 1 *M* perchloric acid. Solutions of spectroscopic grade oxides of the other rare earth oxides in 1 *M* perchloric acid were then examined, using the conditions given on p. 27. The results (Table VI) show that in each case, although there is moderate interference by some

of the least abundant rare earth elements, the commonest rare earth elements of monazites interfere only slightly.

As a test of the flame photometric method, known amounts of yttrium and ytterbium oxides were dissolved in 10 ml aliquots of a solution containing 50 mg of

TABLE VI

EFFECT OF OTHER RARE EARTHS ON DETERMINATION OF YTTRIUM AND YTTERBIUM BY FLAME PHOTOMETRY

Element	*% of oxide*	*Emission at 613.2 mμ (0.2% Y_2O_3 = 100.0)*	*Emission at 398.9 mμ (0.2% Yb_2O_3 = 100.0)*
Er	2.0	7.1	21.0
Dy	1.0	15.4	11.0
Gd	2.0	140.0	23.1
Ho	2.0	4.7	14.4
La	2.0	2.8	9.2
Nd	2.0	14.3	16.1
Pr	1.0	4.5	7.5
Sm	1.0	43.4	16.5
Tb	2.0	42.7	21.6
Tm	2.0	6.0	15.8
Yb	2.0	6.8	—
Y	2.0	—	10.0

La_2O_3, 30 mg of Nd_2O_3, 10 mg Pr_6O_{11} and 5 mg Sm_2O_3 per 10 ml of 1 *M* perchloric acid. These solutions were then examined by flame photometry; recoveries of 2.07 mg and 4.20 mg of Y_2O_3 were found (2.00 and 4.00 mg Y_2O_3 taken respectively). The recoveries of ytterbium were respectively 0.93 mg and 0.47 mg Yb_2O_3 for weights of 1.00 and 0.50 mg Yb_2O_3 taken.

EXPERIMENTAL

A Unicam S.P. 500 spectrophotometer was used for most of the spectrophotometry described in this paper. An Optika CF4 spectrophotometer was, however, used for the determination of the rare earth elements, both by flame photometry and by absorption.

Before analysis, the sample should be well mixed and a representative sample ground to pass a 100-mesh sieve and dried at 110°.

Sulphuric acid attack on mineral

Weigh out accurately about 1.0 g of the finely ground monazite (dried at 110°) into a platinum crucible. Add 5 ml of concentrated sulphuric acid. Heat the covered crucible to *ca.* 250° on a hot plate for 3 h. When cool, quantitatively transfer its contents to a 250 ml beaker containing *ca.* 100 ml of water, using a jet of water. Warm the beaker on a hot plate for 10 min until the solution is clear. Add a small amount of macerated filter paper and stir for a few minutes. Cool, allow the filter pulp to settle and filter through a 12.5 cm hardened filter paper (Whatman No. 542), using gentle suction. The filtrate should be completely clear. Wash the filter with *ca.* 100 ml of water. Combine the filtrate and washings and dilute to *ca.* 400 ml. Use this solution for the determination of the acid-soluble cations. Ignite the filter containing the

insoluble minerals in a tared platinum crucible at 800°. Reweigh the crucible when cold. Reserve the residue for the analysis of the acid-resistant minerals.

Ion exchange of sulphuric acid digest

Preparation of ion-exchange resin column

Elute Zeocarb 225 resin, cross-linked with 8% divinylbenzene (52–100 mesh) with water to remove "fines" and then heat it on the water bath with 3 *M* hydrochloric acid for 1 h to remove iron. Decant the acid, and repeat the acid washing twice. Free the resin from acid by repeated washing with water and store it in the moist condition.

The ion-exchange tube used was constructed of 1.3 cm bore Pyrex tubing. It was constricted at its lower end, and a 46 cm column of the ion-exchange resin was supported on a glass wool plug. The flow rate of the packed column was 60 ± 10 ml/h.

Eluting reagents

Hydrochloric acid (1 and 3 N). Dilute 366 and 1098 ml respectively, of constant-boiling hydrochloric acid (distilled in an all-glass apparatus) to 2 l with redistilled water.

Sulphuric acid (ca. 3.6 N). Dilute 200 ml of concentrated sulphuric acid to 2 l.

Ion exchange

Allow the solution of the sulphuric acid digest from the monazite (volume *ca.* 400 ml) to pass through the ion-exchange column. Wash the column with 3 l of water to remove phosphate. Reject the percolate and washings. Elute with 1970 ml of 1 *N* hydrochloric acid; collect the eluate in a 2 l graduated flask and dilute to volume (this is solution A). Add 2 ml of 60% w/v perchloric acid to 1.0 l of this solution and evaporate to dryness in a silica beaker. Heat on a hot plate until dense white fumes are evolved. Add 2 ml of 60% w/v perchloric acid and 30 ml of water, warm on the water bath until all the solid has dissolved and dilute to 100 ml (this is solution B).

Elute the rare earth elements from the column using 750 ml of 3 *N* hydrochloric acid. Evaporate this eluate almost to dryness in a silica beaker on the water bath. Evaporate the residue twice to dryness with 10 ml portions of concentrated nitric acid to remove chlorides. Take up the residue in 25 ml of 8.5 *N* nitric acid and use for the separation of cerium from other rare earth elements (p. 19).

Finally, elute thorium from the column using 800 ml of 3.6 *N* sulphuric acid. Dilute the eluate to 1 l. Evaporate 25 ml aliquots to dryness in Pyrex beakers under an infra-red heater. Take up the residue in 1 ml of 60% perchloric acid and 20 ml of water, and dilute to 50 ml in a volumetric flask. Determine thorium in this solution as described on p. 20.

Analysis of 1 N hydrochloric acid eluate

(1) Determination of aluminium

Reagents

Complexing reagent. Mix 4 ml of 25% w/v hydroxyammonium chloride solution, 50 ml of 1 *M* sodium acetate and 20 ml of dipyridyl solution (0.2 g of 2,2'-dipyridyl in 100 ml of 0.02 *N* hydrochloric acid), and dilute to 100 ml.

8-Hydroxyquinoline reagent. Dissolve 1.25 g of 8-hydroxyquinoline A.R. in 250 ml of chloroform A.R.

Anion exchanger. Shake 10 g of Amberlite IRA400 (Cl) (80 mesh) with 100 ml of 2 *M* sodium acetate for 20 min. Allow the resin to settle and decant the supernatant liquid. Wash the resin with water. Fill an ion-exchange column *ca.* 0.8 cm in diameter, with enough of the resin to give a 12 cm layer.

Standard aluminium solution. Dissolve 0.0529 g of spectrographic grade aluminium (99.99% Al) in a slight excess of dilute hydrochloric acid and dilute to 2 l. This solution contains the equivalent of 50 μg Al_2O_3/ml.

Procedure

Pipette 5 ml of solution B into a 25 ml conical flask and add 5 ml of 1.0 *M* sodium acetate trihydrate. Pour the mixture into the ion-exchange column, and rinse the flask into the column with small volumes of water (total volume *ca.* 15 ml). Collect the percolate and washings in a 50 ml separating funnel. Add 10 ml of the complexing reagent. After 5 min add 20 ml of 8-hydroxyquinoline reagent. Shake the separating funnel mechanically for 5 min. Run the chloroform layer through a small filter paper into a dry 25 ml graduated flask. Pour 2–3 ml of chloroform into the separating funnel, and shake it gently, pass the chloroform through the funnel into the flask. Dilute to volume with chloroform. Measure the optical density of the solution at 410 mμ in a covered 1 cm cell against chloroform contained in the compensator cell. Carry out a blank determination using distilled water instead of solution B. Standardise the method using 2 ml of standard aluminium solution.

Since the aluminium complex is somewhat sensitive to light, the extraction must be carried out in a dimly lit room, and the extracts stored in a dark cupboard until they are measured.

(2) Determination of calcium and magnesium

Reagents

Ethylenediaminetetraacetic acid (EDTA). Dissolve 0.25 g of EDTA (di-sodium salt) and 10 mg of hydrated magnesium chloride in 1 l of water.

Ammonia–ammonium chloride buffer. Dissolve 70 g of ammonium chloride in 600 ml of ammonia solution (s.g. 0.88) and dilute to 1 l with water.

Standard calcium solution. Dissolve 0.8925 g of calcium carbonate A.R. (dried at 110°) in a slight excess of dilute hydrochloric acid. Dilute to 1 l. This solution contains the equivalent of 500 μg CaO/ml.

Standard magnesium solution. Dissolve 0.3015 g of spectrographic grade magnesium (99.99% mg) in dilute hydrochloric acid. Dilute to 2 l. This solution contains the equivalent of 250 μg MgO/ml.

Procedure

Removal of interfering elements. Pipette 25 ml of solution B into a 100 ml conical flask, add, with shaking, 3 ml of 2 *M* sodium acetate, and 1 ml of 20% w/v 8-hydroxyquinoline in acetone. Extract the mixture with chloroform in a continuous extractor[20] until the solution is clear and colourless. Transfer the liquid to a 50 ml separating funnel. Run off the lower (chloroform) layer and filter the aqueous layer through a 9 cm Whatman No. 41 filter paper into a 100 ml graduated flask. Thoroughly wash the separating funnel and filter and dilute to volume.

Titration of calcium. Pipette 25 ml of the extracted solution into a 50 ml titration beaker, add 0.5 ml of the standard magnesium solution, 5 drops of 50% v/v triethanolamine in water and 3 ml of diethylamine (redistilled). Stir the resultant solution, which should have a pH of *ca.* 12.5, for 3 min to assist the precipitation of magnesium hydroxide. Add 0.5 ml of calcon (1-(2-hydroxy-4-sulphonaphthylazo)-2-naphthol) indicator (0.2% w/v in methanol) and titrate the solution photometrically with EDTA solution, using an orange filter (maximum transmission at *ca.* 600 mμ, *viz.* Ilford Filter No. 607). The colour change at the end-point is from pink to a pure blue-green colour.

Titration of calcium + magnesium. Place 12.5 ml of the extracted solution into a 50 ml titration beaker. Add 10 ml of water, *ca.* 10 mg of ascorbic acid, 5 drops of 50% w/v triethanolamine in water, 1 ml of ammonia–ammonium chloride buffer, and 0.5 ml of an ethanolic 0.2% Eriochrome Black T solution. Titrate the solution photometrically with EDTA solution, using an orange filter, similar to that used in the titration of calcium. The colour changes at the end-point from pink to a pure blue-green.

Standardisation of EDTA. Carry out extractions on distilled water containing 10 ml of standard calcium solution, and on distilled water containing 20 ml of the standard magnesium solution. In each case, add before extraction, 2 ml of 2 *M* sodium acetate and 1 ml of the 8-hydroxyquinoline solution. Dilute the extracts to 100 ml. Titrate 10 ml aliquots of the extracted calcium and magnesium solutions with EDTA using Eriochrome Black T indicator. Titrate 10 ml of the extracted calcium solution with EDTA using calcon as indicator, after adding 0.5 ml of the standard magnesium solution. Determine the reagent blank by carrying out an extraction in the same manner, using distilled water and titrating 10 ml aliquots with EDTA, using the two indicators.

(3) Determination of iron

Reagents

Dipyridyl reagent. The same reagent as that used as complexing reagent in the determination of aluminium, p. 15.

Standard iron solution. Dissolve 0.1398 g of spectrographic grade iron sponge in 5 ml of 2 *N* hydrochloric acid and dilute to 2 l. This solution contains the equivalent of 100 μg Fe_2O_3/ml.

Procedure

Pipette 5.0 ml of solution B into a 50 ml graduated flask. Add 10 ml of the dipyridyl reagent and dilute to volume. Measure the optical density of the solution in a 1 cm cell at 522 mμ. Standardise the method with 2 ml of the standard iron solution. Prepare a reagent blank using distilled water and the dipyridyl reagent.

(4) Determination of lead

Reagents

All reagents and solutions used in the analysis should be prepared using water distilled from a glass or silica still.

Ammonium citrate. Dissolve 50 g of ammonium citrate in 100 ml of water. Add a few drops of thymol blue indicator and treat the solution gradually with 10 *N*

ammonium hydroxide until the indicator turns blue. Remove lead by extracting with a 0.005% solution of dithizone in carbon tetrachloride. Repeat the extraction until the organic phase remains green. Extract once with carbon tetrachloride. Filter the aqueous phase through a Whatman No. 41 filter paper and store in a Pyrex glass bottle.

Dithizone 0.001%. Dissolve 5.0 mg of dithizone in 500 ml of carbon tetrachloride. Filter the solution before use. Store in a refrigerator.

Standard lead solutions. Dissolve 0.1484 g of lead nitrate A.R. in water and dilute to 1 l. This solution contains the equivalent of 100 μg PbO/ml; prepare from it, as required, a working standard containing 5 μg PbO/ml.

Procedure

Place 5 ml of solution A in a 50 ml separating funnel, containing 10 ml of water. Add 5 ml of ammonium citrate solution, 1 ml of 20% w/v hydroxyammonium chloride solution, 2 ml of ammonia solution (s.g. 0.88) and 1 ml of 10% w/v potassium cyanide solution. Mix gently and add, from a pipette, 10 ml of dithizone reagent. Shake the separating funnel vigorously for 1 min. Allow the two phases to separate. Run off and discard a few drops of the lower layer, dry the stem of the funnel and then run the lower layer into a 10 ml stoppered flask. Measure the optical density of the extract at 520 mμ in a 1 cm cell against a compensator cell containing carbon tetrachloride. Carry out a reagent blank determination in the same manner, but omitting the sample. Calibrate the method using 10 μg of PbO. BEER's law is obeyed up to *ca.* 13 μg PbO, but above this level there is a marked deviation owing to the rather small solubility of lead dithizonate in the solvent.

(5) Determination of titanium

Reagents

Hydrogen peroxide reagent. Mix 200 ml of 50% v/v sulphuric acid, 200 ml of phosphoric acid (88%) and 200 ml of 100-volume hydrogen peroxide. Dilute to 1 l with distilled water.

Standard titanium solution. Weigh into a 100 ml conical flask 0.4433 g of potassium titanium oxalate, and add 10 ml of concentrated sulphuric acid. Heat the flask on the hot plate until dense white fumes are evolved. When cold, dilute to 1 l. This solution contains 100 μg TiO_2/ml.

Procedure

Pipette 20 ml of solution B into a 25 ml graduated flask and dilute to volume with the hydrogen peroxide reagent. Measure the optical density of the solution at 400 mμ in a 4 cm cell. Determine the reagent blank using 20 ml of distilled water. Calibrate the method using 4 ml of the standard titanium solution. Uranium interferes slightly in the determination. The corrected optical density, D_c, can be calculated from the following equation:

$$D_c = D_o - 0.012 \cdot \% \ U_3O_8$$

in sample, where D_o is the observed optical density at 400 mμ in a 4 cm cell.

(6) Determination of uranium

Reagents

Dibenzoylmethane reagent. Dissolve 0.4 g of redistilled dibenzoylmethane in 100 ml

of redistilled pyridine, add 2.5 g of ethylenediaminetetraacetic acid (free acid) and dilute to 200 ml with water. Filter if necessary, and store the reagent in the dark.

Standard uranium solution. Dissolve 0.3022 g of uranyl acetate (gravimetrically standardised by precipitation as oxinate) in water, and dilute to 1 l. This solution, which contains the equivalent of 200 μg U_3O_8/ml, is used for the preparation of a working standard solution containing 20 μg U_3O_8/ml.

Procedure

Pipette 5 ml of solution B into a 50 ml separating funnel, add 9.5 g of hydrated aluminium nitrate and 0.2 ml of concentrated nitric acid. Shake until all the solid has dissolved. Add 10 ml of ethyl acetate (A.R.), shake for 1 min and allow to stand until the organic phase has become clear. Run off the aqueous phase and filter the ethyl acetate through a 5.5 cm Whatman No. 1 filter paper. Collect the filtrate in a 30 ml beaker. Re-extract the aqueous phase with a further 5 ml of ethyl acetate, and filter the extract through the same filter. Evaporate the combined extracts under an infrared heater. Add a few drops of perchloric acid to the residue and fume to dryness to remove any traces of organic material.

Add 0.1 ml of concentrated hydrochloric acid to the beaker and wash it with four 0.5 ml portions of distilled water. Using a dropper, transfer the washings to a dry 10 ml graduated flask. Add 0.5 ml of tartaric acid solution (50 g dissolved in water and diluted to 100 ml) and dilute to volume using dibenzoylmethane reagent. Measure the optical density of the solution at 415 mμ, using cells of an appropriate length. Calibrate the method by extracting 5 ml aliquots of standard uranium solution (equivalent to 80 μg U_3O_8 for 1 cm cells) and carry out the determination as described above. Determine the reagent blank in the same manner using 5 ml of distilled water.

(7) Determination of manganese

Reagents

Acid reagent. Dissolve 18.7 g of mercuric sulphate in a mixture of 100 ml of concentrated nitric acid and 50 ml of water. Add 50 ml of 87% phosphoric acid and 8 mg of silver nitrate. Dilute to 250 ml with water.

Standard manganese solution. Dissolve 0.0774 g of pure manganese in 20 ml of 0.5 *N* sulphuric acid, and dilute to 2 l with water. This solution contains the equivalent of 50 μg MnO/ml.

Procedure

Pipette 20 ml of solution B into a 50 ml conical flask, and add 1.5 ml of the acid reagent and *ca.* 0.5 g of ammonium persulphate. Place the flask on the hot plate and boil for 1 min. Cool the solution to room temperature under the tap and dilute to 25 ml. Measure the optical density of the solution at 525 mμ in a 4 cm cell. Determine the reagent blank using 20 ml of distilled water. Calibrate the method using 2 ml of the standard manganese solution.

Analysis of 3 N hydrochloric acid eluate

Separation of cerium from other rare earth elements

Reagents

Methyl iso-butyl ketone. Equilibrate by shaking with an equal volume of 8.5 *N* nitric acid and a small amount of sodium bromate.

Procedure

Transfer the solution of the rare earth elements in 25 ml of 8.5 *N* nitric acid (p. 15) to a 250 ml separating funnel, using a further 25 ml of 8.5 *N* nitric acid. Add *ca.* 0.5 g of sodium bromate, and extract with 100 ml of methyl iso-butyl ketone for 2 min. Draw off the nitric acid phase into a 100 ml beaker. Pour the organic phase, via the top of the separating funnel, into a 250 ml separating funnel containing 25 ml of 8.5 *N* nitric acid. After shaking for 2 min, transfer the ketone phase to a 500 ml separating funnel containing 100 ml of water and 1 ml of 100-volume hydrogen peroxide. Re-extract the first nitric acid phase with a further 100 ml of ketone, followed by four extractions with 50 ml of the ketone. In each case wash the extract with the 25 ml aliquot of 8.5 *N* nitric acid, to remove any entrained or extracted rare earths. Quantitatively transfer the two nitric acid phases to a beaker, evaporate to dryness on the water bath and use the residue for the determination of rare earths less cerium.

Shake the separating funnel containing the combined ketone extracts and dilute hydrogen peroxide to transfer cerium to the aqueous phase. Run off the aqueous phase and wash the ketone twice with water. Combine the aqueous phase and washings and evaporate to dryness on the water bath and use the residue for the determination of cerium.

Determination of cerium and total other rare earths

Dissolve the residues from the evaporations in *ca.* 450 ml of water containing 2–3 ml of concentrated nitric acid. Add 30 ml of a 2% solution of 8-hydroxyquinoline in ethyl alcohol and then add, with stirring, 2 *N* ammonia solution until the solution smells faintly of ammonia. In the case of cerium, heat the solution on the water bath until the yellow-orange cerous oxinate is oxidised to the dark brown ceric compound, and then cool. If the supernatant liquid is not yellow, add more 8-hydroxyquinoline solution. On the following day, using suction, filter the solution through a 12.5 cm diameter Whatman No. 541 filter folded within a No. 542 filter. Transfer the precipitate to the filter with a jet of hot water. Wash the precipitate and filter with hot water. Transfer the precipitate to a weighed platinum crucible; ignite at 700° in a muffle furnace until the residue is free from carbon. Ignite the cerium precipitate at 1000° for 10 min and weigh as the dioxide. Ignite the rare earth oxide precipitate at 1000°, cool in a current of hydrogen and weigh as R_2O_3. The determination of the individual rare earth elements is carried out as described on p. 27 ff.

Determination of thorium in 3.6 N sulphuric acid eluate

Reagents

Thorin solution. Dissolve 0.1 g of thorin (1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid sodium salt) in water, and dilute to 100 ml. Filter before use.

Standard thorium solution. Weigh out an appropriate amount of thorium nitrate A.R. (which has been gravimetrically standardised by ignition to oxide) to give 100 ml of solution containing 500 μg ThO_2/ml. Dissolve it in 0.5 *N* perchloric acid. Prepare a working standard by dilution of 2 ml to 100 ml with 0.1 *N* perchloric acid. This solution, which contains 10 μg ThO_2/ml, should be prepared as required.

Procedure

Pipette into a 25 ml graduated flask a 5 ml (for 5% ThO_2) aliquot of the solution prepared from 25 ml of the 3.6 *N* sulphuric acid eluate (p. 15). Add 2.5 ml of 60% perchloric acid and 5 ml of thorin solution. Dilute to volume with water. Measure the optical density at 547 mμ against a compensating cell containing a reagent blank prepared in the same manner, but omitting thorium. Calibrate the method with 200 μg of ThO_2.

Opening up of sulphuric acid-insoluble residue

To the weighed residue (p. 14) contained in a platinum crucible, add 0.5 g of anhydrous sodium carbonate. Heat the crucible over a Meker burner to bright red heat for 20 min. When cold, gradually add 10 ml of 10% v/v sulphuric acid; after all gas evolution has ceased, add 5 ml of 40% hydrofluoric acid. Warm the closed crucible on the water bath for several hours, and then evaporate the liquid. Continue the evaporation under an infrared lamp. Add 10 drops of concentrated sulphuric acid, and heat the covered crucible to dull redness for 10 min, ceasing the heating while dense white fumes are still being evolved. When cold, add a further 5 drops of sulphuric acid and 10 ml of water. Warm the crucible on the water bath, and when dissolution is complete, dilute to 100 ml. This is solution C.

This process should produce a clear solution. If a white turbidity or visible precipitate is present, this is due to niobium and/or tantalum or tin. If small amounts of these elements are present, add filter pulp and filter through a 9 cm Whatman No. 542 filter. Wash the filter with cold water and ignite in a platinum crucible. Dissolve the niobium and tantalum oxides in hydrofluoric acid and determine them by paper chromatography as described by SCOTT AND MAGEE[66].

Run a reagent blank through the whole process in the same manner, but omitting the sample. This is solution D.

If the sulphuric acid-insoluble residue contains sodium or potassium minerals, digest it with 5 ml of 40% hydrofluoric acid and 3 ml of concentrated sulphuric acid. Evaporate the hydrofluoric acid and heat it until dense white fumes are evolved. Add 30 ml of water and centrifuge; make up to 50 ml, and determine sodium and potassium in the residue as described by RILEY[18]. Fuse the residue with sodium carbonate, continue the remainder of the opening-up process as described above, and dilute to 100 ml. Combine proportionate quantities of these solutions for the determination of other cations.

(1) Determination of iron

Procedure

Pipette a 4 ml aliquot of solution C into a 50 ml graduated flask, add 10 ml of the dipyridyl reagent (p. 17) and dilute to volume. Measure the optical density of the solution in a 4 cm cell at 522 mμ. Determine the reagent blank of the method using 4 ml of solution D. Standardise the method using 50 μg Fe_2O_3; carry out a corresponding reagent blank using distilled water.

(2) Determination of titanium

Reagents

The hydrogen peroxide reagent and standard titanium solution are prepared as described on p. 18.

Procedure

Place 10 ml of solution C in a 25 ml graduated flask. Add 5 ml of hydrogen peroxide reagent and dilute to volume with water. Measure the optical density of the solution at 400 mμ in a 4 cm cell. Determine the reagent blank in the same manner using distilled water instead of solution C. Calibrate the method using 400 μg of TiO_2.

(3) Determination of zirconium

Reagents

Quinalizarinsulphonic acid solution. Dissolve 0.2 g of the sodium salt of quinalizarinsulphonic acid[67] in 500 ml of water. Filter before use.

Standard zirconium solution. Prepare a stock solution containing 500 μg ZrO_2/ml in 0.5 *N* nitric acid. Prepare from it, as required, a working standard containing 15 μg ZrO_2/ml also in 0.5 *N* nitric acid.

Procedure

Pipette 10 ml of solution C into a platinum crucible, evaporate on the water bath, and finally evaporate under an infrared heater to remove sulphuric acid which interferes in the determination of zirconium. Treat the residue with 1 ml of 60% perchloric acid and *ca.* 5 ml of water; warm on the water bath. When all the residue has dissolved, cool, and transfer the solution to a 25 ml graduated flask. Add 1 ml of 10% w/v hydroxyammonium chloride solution, 2.5 ml of quinalizarinsulphonic acid reagent and 5 ml of acetone. Dilute to volume with water. Measure the optical density of the solution in a 1 cm cell at 565 mμ after 3 h. Prepare a reagent blank by treating 10 ml of water with the same amounts of reagents. Calibrate the method using 200 μg of ZrO_2 which has been carried through the evaporation stage. The zirconium complex obeys BEER's law in the range 25–200 μg ZrO_2.

(4) Determination of aluminium, hafnium, calcium and magnesium

Reagents

Ammonium lactate 0.1 M. Dissolve 18.0 g of lactic acid in *ca.* 1.8 l of water, and adjust the pH to 5.8 by the gradual addition of 1.5 *M* ammonia solution (approximately 92 ml is required). Dilute to 2 l.

Hydrochloric acid 3 N. Prepare by dilution of the constant-boiling acid as described on p. 15.

Ion-exchange columns

The ion-exchange columns, which have a diameter of 8 mm, are packed to a height of 14 cm with Zeocarb 225, prepared as described on p. 15.

Ion-exchange separation

Dilute 60 ml of solution C to approximately 200 ml with water and allow it to percolate through the ion-exchange resin. Wash the resin with *ca.* 300 ml of water and reject the percolate and washings. Elute with 300 ml of 0.1 *M* ammonium lactate, collect the eluate in a 500 ml graduated flask, dilute to volume and use for the determination of aluminium. Wash the column until free from lactate.

Elute zirconium and hafnium with 80 ml of 0.05 *M* oxalic acid. Add to the eluate

10 ml of 4% w/v sodium bromate and 2 ml of 60% perchloric acid and allow to stand overnight in order to destroy oxalic acid. On the following morning, add 2 ml of 10% hydroxyammonium chloride solution to remove bromine and excess bromate. Use the solution for the determination of hafnium.

Finally, elute the column with 45 ml of 3 *N* hydrochloric acid. Add 2 ml of perchloric acid to the eluate and evaporate on the hot plate in a silica beaker until copious dense white fumes are evolved. Dilute to 25 ml, and use an aliquot for the determination of calcium and magnesium.

Photometric determination of aluminium

Aluminium is determined using a 20 ml aliquot of the 0.1 *M* ammonium lactate eluate, by 8-hydroxyquinoline extraction, as described on p. 16.

Spectrographic determination of hafnium

Treat the 0.05 *M* oxalic acid eluate (after destruction of oxalic acid with bromate) with 5 ml of 0.2% quinalizarinsulphonic acid. Boil to precipitate zirconium and hafnium. Concentrate the precipitate by centrifugation and then filter it off on to a 6 mm diameter Whatman No. 42 paper covered with 2 mg of pure alumina. Transfer the filter and precipitate to a small platinum crucible and ignite at 800°. Mix the residue with 5 mg of powdered carbon. Arc the mixture using carbon electrodes under the conditions described by WARING AND WORTHING[71]. Determine the hafnium: zirconium ratio from the ratio of the log intensities of the lines Hf 2641 Å and Zr 2583 Å. Calibrate the method using mixtures of known concentrations of HfO_2 in ZrO_2.

Determination of calcium and magnesium

The 3 *N* hydrochloric acid eluate contains part of the iron from the sample, and iron must be removed before the calcium and magnesium are titrated. A 20 ml aliquot of the evaporated 3 *N* hydrochloric acid eluate is therefore extracted as described on p. 16. The titrations of calcium and magnesium are carried out as described on p. 17.

Photometric determination of phosphorus pentoxide in monazite

Reagents

Mixed reagent. Mix 125 ml of 5 *N* sulphuric acid, and 37.5 ml of ammonium molybdate solution (20 g of ammonium molybdate in water diluted to 500 ml). Add 75 ml of freshly prepared ascorbic acid solution (1.76 g in 100 ml of water), dilute to 250 ml and mix well. This solution should be used within an hour of mixing.

Standard phosphate solution. Prepare a solution containing 50 μg P_2O_5/ml from potassium dihydrogen phosphate, which has been gravimetrically standardised. Prepare from it a working standard containing 10 μg P_2O_5/ml.

Treatment of graduated flasks

Graduated flasks to be used for the photometric determination should be allowed to stand overnight filled with concentrated sulphuric acid, and then washed with distilled water.

Procedure

Weigh out accurately about 0.1 g of the finely ground sample into a platinum crucible and add 1 ml of concentrated sulphuric acid. Place the covered crucible on the hot plate and heat it to approximately 250° for 3 h. After cooling, wash the contents of the crucible into a beaker. Warm on the hot plate for 10 min, stir in a small amount of macerated filter paper and then filter the solution through a Whatman No. 542 filter paper. Wash the filter well with hot water. Combine the filtrate and washing and dilute to 2 l.

Place a 5 ml aliquot of this solution in a 50 ml graduated flask, and add 10–15 ml of water and 20 ml of the mixed reagent. Dilute to volume. After not less than 12 h, measure the optical density of the solution at 827 mμ in a 1 cm cell. Carry out a reagent blank determination, using distilled water in place of the monazite solution. Calibrate the method using 5 ml of the standard phosphate solution (50 μg of P_2O_5).

Determination of silica in monazite

Reagents

Acid molybdate solution. Dissolve 2 g of ammonium molybdate in *ca.* 100 ml of water, add 6 ml of concentrated hydrochloric acid and dilute to 250 ml.

Metol–sulphite reagent. Shake 5 g of metol (*p*-methylaminophenol sulphate) with *ca.* 230 ml of water in which 3 g of anhydrous sodium sulphite has been dissolved. After solution is complete, dilute to 250 ml and filter.

Reducing solution. Mix 85 ml of metol–sulphite solution with 50 ml of 10% w/v oxalic acid, add 100 ml of 25% v/v sulphuric acid and dilute to 250 ml.

Standard silica solution (10 μg SiO_2/ml). Fuse 0.02 g of pure silica with 3 g of sodium hydroxide at 700° for 5 min. Dissolve in water, acidify with 25 ml of 2.5 *N* sulphuric acid and dilute to 2 l.

Treatment of graduated flasks

The graduated flasks used for the spectrophotometric determination of silica should be allowed to stand overnight filled with concentrated sulphuric acid. They should be emptied, rinsed several times with water and drained, but should not be allowed to become dry.

Procedure

Weigh out accurately about 0.1 g of the finely ground monazite into a 30 ml silver crucible and add 1.5 g of sodium hydroxide. Place the covered crucible in a muffle furnace at 700° for 10 min. After cooling, add 20 ml of distilled water and warm on the water bath. When the decomposition of the fused mass is complete, pour the contents of the crucible through a polyethylene funnel into a 1 l graduated flask containing *ca.* 200 ml of water and 20 ml of 2.5 *N* sulphuric acid. Rinse the crucible and its lid several times with distilled water. Add 5 ml of 2.5 *N* sulphuric acid and scour it thoroughly with a rubber policeman. Add the washings to the graduated flask and dilute to volume. Allow the precipitated rare earth oxides or hydroxides to settle before determining silica photometrically. Carry out a blank fusion in the same manner, omitting the sample.

Pipette 2 ml of the solution from the fusion of the monazite into a 100 ml graduated

flask. Add about 10–15 ml of water and 10 ml of the acid–molybdate reagent. After 15 min add 15 ml of the reducing solution and dilute to 100 ml. Measure the optical density of the solution at 812 mμ in a 4 cm cell after at least 12 h. Carry out a blank determination on the fusion blank. Standardise the method using 3 ml of the standard silicate solution (30 μg SiO_2).

Determination of tin in monazite

Reagents

8-Hydroxyquinoline. Dissolve 1 g of 8-hydroxyquinoline in 500 ml of chloroform Store in an amber glass-stoppered bottle.

Standard tin solution. Dissolve 0.1269 g of pure tin in 20 ml of 1 *N* hydrochloric acid, dilute to 1 l with 1 *N* hydrochloric acid. This solution contains the equivalent of 100 μg SnO_2/ml.

Procedure

Weigh out 0.5–0.6 g of the monazite into a platinum crucible, add 4 ml of concentrated sulphuric acid and heat to 250° for 2 h. When cold, add 25 ml of water, warm to dissolve the sulphates and centrifuge. Wash the residue with water, combine the centrifugate and washings and retain them. Fuse the insoluble residue in a nickel crucible with 1.5 g of sodium peroxide at dull red heat for 10 min. Leach the fused cake with water, transfer to a beaker, acidify with sulphuric acid and evaporate to small bulk to destroy peroxide. Combine this solution with the centrifugate, add 10 ml of concentrated sulphuric acid and 3 ml of phosphoric acid. Transfer to a distillation apparatus of the type described by SCHERRER[69]. Distil until the temperature of the thermometer immersed in the solution reaches 120°. Reject the distillate. Cool, add 1 g of hydrazine sulphate and 10 ml of concentrated hydrochloric acid. Heat the solution to 140°, and then add dropwise a mixture of 15 ml of 6 *N* hydrochloric acid and 7 ml of 48% hydrobromic acid. The rate of addition should be controlled so that the temperature of the liquid remains between 145° and 160°. Add 0.5 ml of concentrated sulphuric acid and 4 ml of concentrated nitric acid to the distillate and evaporate it to dryness. Add 1 ml of concentrated hydrochloric acid to the residue and warm to dissolve the antimony. Dilute to 25 ml with 0.5 *N* hydrochloric acid.

Pipette 3 ml of this solution (sufficient for 0.5% of SnO_2 in the sample) into a 50 ml separating funnel. Add 10 ml of water, 1 ml of 10-volume hydrogen peroxide and 10 ml of the 0.2% 8-hydroxyquinoline solution. Shake and then add 10 ml of 2 *M* sodium acetate. Shake for 2 min and run off the lower layer through a small filter paper into a 25 ml graduated flask. Re-extract the aqueous phase with 10 ml of 8-hydroxyquinoline solution, combine the two extracts and dilute to volume with chloroform. Measure the optical density of the extract at 385 mμ in a 1 cm cell against a compensator cell containing chloroform. Carry out a blank determination in the same manner, omitting the sample. Calibrate the method with 4 ml of the standard tin solution (400 μg SnO_2).

Determination of chromium in monazite

Reagent

Standard chromium solution. Dissolve 0.1277 g of potassium chromate in water, add 5 ml of 1 *M* sodium carbonate and dilute to 1 l. This solution contains 50 μg Cr_2O_3/ml.

Procedure

Fuse 0.5 g of finely powdered monazite with 4 g of 10 : 1 sodium carbonate–sodium nitrate mixture at a bright red heat for 20 min. Leach with 50 ml of water. Filter the solution through a small filter paper, which has been previously washed with a little hot sodium carbonate solution, and wash the precipitate with hot dilute sodium carbonate solution. Dilute to 250 ml, or 1 l if the amount of chromium is high. Measure the optical density of the solution at 366 mμ. Calibrate the method using the standard chromate solution.

Determination of water in monazite

Monazites generally contain 0.1–0.5% of non-hygroscopic water; this may be determined as described by RILEY AND WILLIAMS[73], with the exception that sample weights of 0.25 g should be taken.

Determination of carbon dioxide in monazite

Pure monazite normally contains less than 0.1% of carbon dioxide, but concentrates of the mineral may sometimes contain up to 0.6% of carbon dioxide associated with carbonate minerals. The analysis for carbon dioxide may be conveniently carried out by the method of GROVES[72].

ANALYSIS OF ARTIFICIAL MIXTURES

Since no monazite samples of accurately known composition were available, the accuracy of the analytical processes described above for the analysis of the sulphuric acid-soluble fraction of monazites was tested using 4 artificial mixtures of known composition. These mixtures (Table VII) contained the various elements in amounts similar to those expected in solutions from monazites. They were prepared from known weights of rare earth oxides and thorium oxide, which had been dissolved in 30 ml of 2 *N* sulphuric acid; appropriate volumes of standard solutions of other elements were also added. The mixtures, after the addition of 0.3 ml of 85% phosphoric acid, were diluted to *ca.* 500 ml and allowed to percolate through the ion-exchange columns. The water washing of the columns, the consecutive elution with 1 *N* and

TABLE VII

ANALYSIS OF ARTIFICIAL MIXTURES (ALL WEIGHTS IN mg)

Oxide	*A*		*B*		*C*		*D*	
	Taken	*Found*	*Taken*	*Found*	*Taken*	*Found*	*Taken*	*Found*
R_2O_3[a]	292.6	293.0	292.6	293.0	292.6	292.2	292.6	292.4
Ce_2O_3	305.3	305.0	305.3	304.7	305.3	304.7	305.3	304.8
ThO_2	83.9	83.7	126.0	125.6	168.0	167.2	210.0	210.4
TiO_2	2.57	2.58	3.86	3.91	5.14	5.20	6.43	6.48
Fe_2O_3	0.615	0.628	2.05	2.04	4.10	4.08	10.25	10.19
Al_2O_3	2.00	1.98	4.00	4.13	6.00	6.04	10.00	9.94
CaO	1.00	1.02	5.00	5.02	10.00	10.14	20.00	20.18
MgO	1.00	1.01	5.00	5.06	10.00	10.12	20.00	20.10
Na_2O	1.15	1.21	2.30	2.24	4.60	4.53	7.20	7.37
PbO	1.07	1.08	2.15	2.17	4.31	4.35	6.46	6.42
U_3O_8	0.59	0.57	1.18	1.14	2.36	2.39	4.72	4.83

[a] Composed of 0.1088 g La_2O_3, 0.0390 g Pr_6O_{11}, 0.0653 g Yb_2O_3 and 0.0795 g Nd_2O_3.

3 *N* hydrochloric acid and 3.6 *N* sulphuric acid, and subsequent analysis of the eluates, were carried out as described above. All titrimetric and photometric determinations were performed in duplicate. The results of these experiments, which are given in Table VII, show that satisfactory recoveries were obtained in every case.

The method developed for the analysis of the sulphuric acid-insoluble residue

TABLE VIII

ANALYSIS OF ARTIFICIAL MIXTURES (ALL WEIGHTS IN mg)

Mixture	*A*		*B*		*C*		*D*	
	Taken	*Found*	*Taken*	*Found*	*Taken*	*Found*	*Taken*	*Found*
Fe_2O_3	5.00	4.95	10.00	9.90	15.00	14.76	20.00	19.50
Al_2O_3	3.00	2.96	6.00	5.92	9.00	9.06	12.00	11.80
TiO_2	3.00	3.04	6.00	6.23	9.00	8.93	12.00	12.29
ZrO_2 + HfO_2	2.50	2.49	5.00	4.99	7.50	7.47	10.00	10.01
CaO	3.00	3.06	6.00	6.03	9.00	9.02	12.00	12.06
MgO	3.00	2.98	6.00	6.14	9.00	8.97	12.00	12.09

was tested by analysing 4 solutions containing known amounts of the elements present in the residue. These solutions, which also contained the same amounts of sodium, sulphate ion and acid as the solutions obtained when the residue was dissolved, were analysed as described on p. 21 ff. The results, which are summarised in Table VIII, indicate that quantitative recoveries are obtained in each case.

Determination of selected rare earths in separated rare earth fraction

Prepare a 2% solution of the freshly ignited mixed rare earth oxides (less cerium) in 1 *M* perchloric acid. Measure the optical density of this solution in a 4 cm cell against 1 *M* perchloric acid at 401.5, 444.2 and 521.9 mμ at bandwidths of 0.15, 0.075 and 0.15 mμ respectively. Calculate the $E^{1\%}_{1cm}$ values at these wavelengths and compute the concentrations of samarium, praseodymium and neodymium using the extinction coefficients given in Table IX.

TABLE IX

$E^{1\%}_{1cm}$ VALUES FOR DETERMINATION OF RARE EARTHS

	401.5 mμ	*444.2 mμ*	*521.9 mμ*	*908.7 mμ*
Nd_2O_3	0.0073	0.0079	0.2640	0.0031
Pr_2O_3	0.0019	0.603	0.0009	0.0007
Sm_2O_3	0.1937	0.0107	0.0032	0.000
Dy_2O_3	0.092	0.000	0.000	1.400

TABLE X

CONDITIONS FOR FLAME PHOTOMETRY

	% Oxide for 100% T	*Wavelength (mμ)*	*Slit (mm)*	*Gain*	*Photocell*	*Gas*	*Gas pressures (kg/cm²)*	
							O_2	*H_2 or C_2H_2*
Lanthanum	0.2	793.2	1.75	11	Red	O_2/C_2H_2	0.22	0.24
Yttrium	0.2	613.2	0.2	11	Blue	O_2/H_2	0.28	0.36
Ytterbium	0.02	398.9	0.3	11	Blue	O_2/H_2	0.28	0.32

Determine lanthanum, yttrium and ytterbium in the solution by flame photometry, using the conditions given in Table X. In the case of lanthanum the determination should be carried out on a 0.2% solution of the mixed oxides. Set the photometer to 100% transmission with solutions of the appropriate Specpure oxides in 1 *M* perchloric acid.

SUMMARY

A scheme using ion-exchange methods is described for the analysis of monazites and monazite concentrates. The sample is opened up with concentrated sulphuric acid, and the resultant solution is applied to a column of Zeocarb 225 resin. After phosphate has been washed out, lead, aluminium, titanium, iron, uranium, calcium and magnesium are eluted with *N* hydrochloric acid and determined by specific, mainly spectrophotometric, methods. Rare earth elements are eluted with 3 *N* hydrochloric acid. Cerium is separated from the other rare earths by solvent extraction of its nitrate with methyl iso-butyl ketone; both groups are determined gravimetrically. Thorium is eluted from the ion-exchange resin with 3.6 *N* sulphuric acid and determined spectrophotometrically with thorin.

The sulphuric acid-insoluble minerals are brought into solution by a double fusion method, and the determinations are carried out by a combination of ion-exchange and photometric procedures.

Silica, phosphorus pentoxide, tin and chromium are determined by photometric methods, using separate portions of the sample.

Lanthanum, yttrium and ytterbium are determined in a 1 *M* perchloric acid solution of the mixed rare earth oxides (less cerium) using flame photometry. Samarium, praseodymium and neodymium are determined by spectrophotometry.

RÉSUMÉ

Une méthode est décrite pour l'analyse de monazites et de concentrés de monazites, au moyen d'échangeurs d'ions. Après élimination du phosphate, le plomb, l'aluminium, le titane, le fer, l'uranium, le calcium et le magnésium sont élués par HCl *N* et dosés généralement par spectrophotométrie. Les éléments des terres rares sont élués au moyen d'HCl 3 *N*. Le cérium est séparé des autres terres rares par extraction de son nitrate dans la méthylisobutylcétone, tandis que le thorium est élué par H_2SO_4 et dosé spectrophotométriquement par le thorin.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Analyse von Monaziten mit Hilfe von Ionenaustauscherharze. Nach Entfernung von Phosphat werden Blei, Aluminium, Titan, Eisen, Uran, Calzium und Magnesium mit 1 *N* Salzsäure eluiert und nach spezifischen Methoden bestimmt. Durch Eluierung mit 3 *N* Salzsäure werden dann die seltenen Erden erhalten. Nach Abtrennung des Cers durch Lösungsmittelextraktion werden Lanthan, Yttrium und Ytterbium durch Flammenphotometrie, Samarium, Praseodym und Neodym spektrophotometrisch bestimmt. Silizium, Phosphor, Zinn und Chrom werden in einer besonderen Probe bestimmt.

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DOSAGE DE TRACES DE VITAMINES B_{12}

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La vitamine B_{12} est la seule vitamine renfermant du cobalt. Son effet in vivo est essentiellement catalytique, aussi n'existe-t-elle, le plus souvent, qu'à l'état de traces dans les milieux biologiques, ainsi du reste que dans la plupart des produits pharmaceutiques. C'est pourquoi nous nous sommes efforcé de mettre au point une méthode rapide et précise permettant de doser des quantités de l'ordre de 5 à 10 μg de cette substance. Le poids moléculaire élevé de cette vitamine (1355.42) ne facilite pas la solution du problème.

L'étude bibliographique montre que les méthodes microbiologiques sont certainement les plus sensibles et de beaucoup (0.01 à 0.16 ng/ml)[1]. Mais la durée du dosage, les difficultés qu'il présente, les aléas inhérents à toute méthode catalytique, parfois même la très grande sensibilité qui n'est pas toujours avantageuse, font qu'on ne peut pas l'utiliser dans tous les cas.

Parmi les méthodes chimiques et physico-chimiques en usage, le dosage colorimétrique direct de la B_{12} n'est ni suffisamment sensible ni suffisamment sélectif pour nous. Certains auteurs séparent les substances gênantes sur résines[2,3]. D'autres, par contre-courant[4] ou encore par extraction du dérivé dicyano-cobalamine[5]. Une méthode indirecte de dosage a été proposée[6] qui s'effectue sur les produits d'estérification de l'hydrolysat de la B_{12} par l'alcool octylique.

BOXER ET RICKARDS[7] dosent le 5,6-diméthyl-benziminazole présent dans la molécule de la vitamine B_{12} en la transformant en 4,5-diméthyl-*o*-phénylène-diamine. Avec l'acétylacétone on effectue un dosage colorimétrique et avec l'alloxane un dosage fluorimétrique. Ces méthodes permettent de doser jusqu'à 10 μg de benziminazole (soit de 100 μg de vitamine).

Les mêmes auteurs[8] ont dosé le cyanure, qui constitue le 2% du poids moléculaire de la vitamine B_{12}, par deux méthodes colorimétriques différentes, après libération quantitative de celui-ci. Dans l'une des méthodes le groupement CN est libéré par réduction de la B_{12} au moyen de l'acide hypophosphoreux à 100°; dans l'autre le cyanure se dégage lorsqu'on expose cette vitamine à la lumière, à la température du laboratoire. Malheureusement plusieurs milieux biologiques dégagent aussi du cyanure même en l'absence d'agents réducteurs. Cette méthode n'est donc pas sélective.

La vitamine B_{12} donne un saut polarographique ($E_{\frac{1}{2}} = 1.53$ V *vs.* E.C.S.) pour des concentrations comprises entre 0.005 et 0.02 μg/ml. Mais la reproductibilité est insuffisante et la méthode peu sûre; elle n'est donc pas utilisée.

BACHER, BOLEY ET SHONK[9] ont mis au point une méthode de dosage spécifique

de la vitamine B_{12}, qui comprend plusieurs extractions, un passage sur colonne, pour éliminer complètement les pigments rouges, et un dosage spectrophotométrique. Les pertes inévitables qui se produisent au cours des diverses opérations du dosage sont déterminées par l'addition de vitamine B_{12} marquée au ^{60}Co. Cette méthode est très spécifique mais peu sensible; elle nécessite un minimum de 100 μg de vitamine B_{12} et la déviation standard est de 4.3%.

La méthode que nous proposons consiste à doser colorimétriquement le cobalt de la vitamine B_{12}, par le nitroso-sel R. Pour ce faire celle-ci est détruite, après élimination des substances gênantes (en particulier du cobalt ionique).

PARTIE EXPÉRIMENTALE

Appareillage

Les déterminations spectrophotométriques ont été effectuées au moyen d'un spectrophotomètre Beckman DU, avec photomultiplicateur permettant l'extension de la zone de lecture à 90–100 % sur toute la longueur de l'échelle. Nous avons aussi utilisé le photomètre Eppendorf à lampe de mercure.

Les mesures de la radioactivité ont été faites:

(*1*) avec une échelle décadique Tracerlab, type SC 33 A-1000 Scaler, équipée d'une sonde à scintillation P20B avec un cristal NaI (Tl) à puits, ou d'un tube Geiger TG-C-2 muni d'une fenêtre d'une épaisseur de 2 mg/cm^2;

(*2*) avec une échelle décadique Landys et Gyr, type EL B2, équipée d'un compteur à scintillation type Elko EQP1 ou d'un tube G.M., type EQB1, avec fenêtre en mica d'une épaisseur de 2 mg/cm^2.

Les spectres gamma ont été obtenus au moyen du spectromètre gamma SAIP, à un canal, modèle SPI 3, avec sonde à scintillation équipée d'un cristal plat NaI (Tl) $2'' \times 2''$.

Solutions utilisées

Solution de cobalt radioactif. Sous forme de $^{60}CoCl_2$ renfermant 0.5 μg/ml de Co et ayant une activité de $6.1 \cdot 10^{-2}$ μc/ml.

Solution de vitamine B_{12} d'activité spécifique. 0.5 μc/ml, renfermant 0.5 μg/ml de B_{12}.

Solution de chlorure de cobalt. 0.589 μg Co/ml.

Solutions de vitamine B_{12} pure. Préparées aux concentrations 10 μg/ml, 20 μg/ml et 100 μg/ml.

Solution tampon pH 4. 60 g d'acide citrique et 65 g de citrate de sodium sont dissous dans l'eau bidistillée, on complète au litre. Le pH 4 est ajusté si nécessaire, au moyen d'une solution concentrée de NaOH ou d'acide citrique.

Solution tampon pH 6. Solution aqueuse de CH_3COONa 10 % porté au pH 6 par addition d'acide acétique.

Solution de NaCl 2 %.

Solution aqueuse de nitroso-sel R (N.S.R.). 0.05 g/100 ml.

Acide perchlorique concentré. D = 1.67.

Acide nitrique concentré.

Acide chlorhydrique fumant.

Solution de KCN 10 %.

Solution éluante pour la vitamine B_{12}. 60 ml de dioxane–40 ml HCl 0.25 *N*.

Acétone.

Résine Amberlite CG 50. Rohm & Haas, 100–150 mesh.

Les produits utilisés sont tous des produits Merck pro-anal, sauf les solutions radioactives et celles de la vitamine B_{12} qui proviennent soit de la Maison Hoffman la Roche soit de Merck, New-Jersey.

Détermination des activités

Une petite éprouvette vide de 35 mm de hauteur et de 5 à 7 mm de diamètre est introduite dans le creux du cristal et on détermine le bruit de fond en prenant la moyenne de 5 mesures (d'une minute chacune). On introduit 2 ml de la solution à mesurer dans l'éprouvette et on détermine l'activité. On mesure l'activité du tube vide après rinçage, ce qui permet de calculer l'activité du traceur introduit dans la solution. Chaque activité donnée (en c.p.m., bruit de fond déduit) correspond à une moyenne de 5 mesures (de 1 min chacune).

Afin d'augmenter encore la précision et la sûreté de la méthode, on décèle les variations éventuelles de la géométrie et du rendement du compteur, durant l'analyse, au moyen d'un tube étalon dont on détermine l'activité après chaque mesure faite sur l'échantillon.

Dosage indirect de la vitamine B_{12}

Le dosage spectrophotométrique du cobalt au moyen du nitroso-sel R est extrêmement sensible (0.01 μg/ml). Bien que la B_{12} ne renferme que le 4 % de son poids de cobalt, le dosage de ce dernier est encore, du point de vue chimique, un des meilleurs et des plus sensibles pour déterminer cette vitamine; il est évident que cette méthode n'est valable que s'il ne reste pas de traces de cobalt ionique avec la vitamine (v. p. 34) et s'il n'y a pas dans le mélange des produits d'hydrolyse inactifs de la vitamine B_{12} renfermant du cobalt.

Destruction de la vitamine. Elle a pour but de libérer le cobalt et de détruire les acides rouges, groupements constitutifs de la vitamine B_{12}, qui gênent le dosage par leur coloration.

L'attaque à l'acide nitrique concentré, suivie d'une évaporation à l'infra-rouge, ne donne pas de résultats reproductibles, soit parce que la vitamine n'est pas détruite complètement, soit parce que les produits de décomposition provoquent des interférences. Nous avons constaté par exemple que certains d'entre eux confèrentune légère teinte jaunâtre à la solution. Il faut donc procéder à la destruction totale de la vitamine avec l'acide perchlorique. Pour déterminer les pertes en cobalt qui se produisent au cours de cette opération, nous avons effectué des recherches systématiques avec la B_{12} marquée au ^{60}Co. Ces pertes sont dues surtout à l'adsorption du cobalt sur la paroi des récipients; on peut les diminuer sensiblement en ajoutant à la solution initiale d'importantes quantités d'un électrolyte indifférent; une solution de NaCl 2 % par exemple.

Remarques. Nous avons préféré le NaCl au KCl car ce dernier donne, au cours de la destruction de la B_{12}, du $KClO_4$ peu soluble dans l'eau. Pour le transformer en KCl on doit procéder à plusieurs évaporations à sec en présence de HCl concentré.

Nous nous sommes assurés de la décomposition totale de la vitamine B_{12} en traitant parallèlement et de la même façon, une solution de $CoCl_2$ renfermant la même quantité de cobalt. L'opération de destruction ne provoque pas de pertes sensibles

en cobalt, du moins pour des quantités de vitamine de l'ordre de 2 μg. Un contrôle par indicateur radioactif a donné les mêmes résultats.

Le Tableau I donne la courbe d'étalonnage et l'étude statistique de la méthode.

TABLEAU I

COURBE D'ÉTALONNAGE ET ERREURS STATISTIQUES

B_{12} μg/ml	10	8	5	4	3	2
Densité optique moyenne	0.07	0.056	0.036	0.028	0.0201	0.0135
Ecart type	—	—	0.001	0.00173	0.0016	0.00109
Limite de confiance 95%	—	—	0.0023	0.00398	0.0368	0.0025

TABLEAU II

RÉSULTATS DE MACRO ET MICRODOSAGES

Quantité de B_{12} (μg)	Densité optique obtenue			Valeurs trouvées B_{12} (μg)	Erreurs relatives	Erreurs extrêmes %	
	Min.	Max.	Moy.			Min.	Max.
Macro-dosage: Volume final de 10 ml							
10	0.0685	0.072	0.0700	9.99	±0.01	−1.5	+2
8	0.0545	0.058	0.0558	7.99	±0.01	−2.5	+3.7
5	0.0340	0.037	0.0360	5.15	±0.015	−3	+5.5
4	0.0265	0.0315	0.0285	4.10	±0.1	−5	+10
3	0.0175	0.021	0.0201	2.80	±0.2	−13	0
2	0.0125	0.015	0.0135	1.95	±0.05	−10	+7.5
Semi-micro dosage: (1) Volume final de 5 ml							
6	0.0400	0.042	0.0410	5.90	±0.1	−4.1	0.00
4	0.0245	0.0285	0.0265	3.80	±0.2	−10	+2.5
2	0.0130	0.0145	0.0140	2.00	±0.001	−6.5	+4
(2) Volume final de 2.5 ml							
6	0.0395	0.042	0.0410	5.90	±0.1	−5	0.00
4	0.0245	0.028	0.0268	3.90	±0.1	−10	0.00
3	0.0200	0.024	0.0215	3.05	±0.05	−4.2	−12.0
2.4	0.0135	0.015	0.0142	2.05	±0.05	0.0	−7.5
2	0.0150	0.016	0.0160	2.30	+0.1	−10.3	−4.1

Chaque valeur de la 2e ligne du Tableau I est la moyenne de 10 expériences différentes.

Le Tableau II donne le résultat d'un certain nombre de dosages macro et semi-micro avec les erreurs relatives et absolues. Les colonnes (2) et (3) du Tableau II donnent les valeurs extrêmes obtenues sur 5 dosages. L'erreur % a été calculée en se basant sur les densités optiques extrêmes.

Le dosage de si petites quantités de vitamine B_{12} exige, pour que les résultats soient utilisables, un contrôle très sévère, tant en ce qui concerne les pertes que les contaminations qui se produisent au cours des diverses opérations analytiques auxquelles on soumet l'échantillon.

Pour éliminer les erreurs dues à la contamination en cours d'analyse nous avons, comme il a été indiqué, fait usage d'un blanc. D'autre part les pertes ont pu être exactement déterminées par l'emploi d'un indicateur radioactif: la vitamine B_{12} marquée au ^{60}Co. Une série d'essais nous ont montré qu'elles étaient négligeables.

Essais	*1*	*2*	*3*
Activité initiale de la vitamine B_{12}	1790	1823	1725
Activité du complexe Co–N.S.R.	1740	1885	1675

Etude de la séparation: vitamine B_{12}–ions cobalt

Comme nous venons de le voir, on peut doser quelques μg de B_{12} par la détermination spectrophotométrique du cobalt qui la constitue. Or beaucoup de produits pharmaceutiques renferment des traces de B_{12} de l'ordre du μg en présence de 5000 à 10000 fois plus de cobalt ionique, pour une stabilisation problématique des solutions la renfermant ou pour la nécessité d'une bonne nutrition. La méthode de dosage proposée ne pourra donc s'appliquer à de tels produits que si on dispose d'une méthode de séparation vitamine B_{12}–ions cobalt, rigoureusement quantitative. En effet 10 μg de B_{12} renferme 0.4 μg de cobalt, il faut donc qu'après la séparation, la quantité de cobalt ionique qui reste avec la B_{12} soit inférieure au 1/500 ième du poids de cette dernière. L'étude de cette opération a été considérablement facilitée par l'emploi d'indicateurs radioactifs à base de cobalt-60: le $^{60}CoCl_2$ d'une part et la vitamine B_{12} marquée au cobalt-60 d'autre part. Mais cette séparation n'est possible que s'il n'y a pas d'échange dans les solutions entre le cobalt ionique et le cobalt fixé sur la B_{12}. BALDWIN *et al.*[11] l'affirment ainsi que FANTES[12]. BOOS[13] par contre n'est pas de cet avis. Nous avons montré que, même après une année, il n'y a pas d'échange décelable entre ces particules.

Principe de la séparation. Elle se fait par échangeurs d'ions sur résine Amberlite X E 97 ou CG 50. La B_{12} est retenue dans la partie supérieure de la résine, l'ion cobalt passe dans la solution. Après lavage de la colonne avec du HCl 1 *N*, la B_{12} est éluée par le dioxane. La séparation devant être rigoureusement quantitative, une étude minutieuse des conditions de travail, du mode opératoire et du rendement de l'opération a été nécessaire.

Préparation de la résine. On laisse tremper la résine pendant une nuit dans l'eau distillée, puis on la met en suspension dans ce même milieu. Après dix minutes on décante et on jette l'eau surnageante. Cette opération est répétée dix fois pour éliminer les particules trop fines. La résine est alors introduite dans une colonne de verre de 30 cm de long et 1 cm de diamètre jusqu'à ce qu'elle atteigne une hauteur de 7 à 8 cm. On lave avec NaOH afin que l'éluat soit alcalin et on laisse en contact avec cette dernière pendant 30 min. L'excès d'alcali est éliminé par rinçage à l'eau distillée et on ajoute une solution de pH 4 (v. p. 31) jusqu'à saturation de la résine, puis un excès de 50 ml. Après agitation, on laisse déposer la résine. L'excès de tampon est éliminé jusqu'à ce qu'il ne reste plus que 1 à 2 ml de solution au dessus de la résine, la colonne est ainsi prête à l'emploi.

Séparation vitamine B_{12}–ions cobalt marqués au cobalt-60. On introduit dans un ballon jaugé de 10 ml: 2 ml de la solution KCN (p. 31), 1 ml de la solution de $CoCl_2$ marquée et 2 ml de la solution de B_{12}. On ajuste au pH 7.5 avec la solution d'acide citrique et on complète à 10 ml par addition d'eau bi-distillée. On obtient ainsi la solution A. La solution B sera préparée de façon identique mais sans vitamine B_{12}. On laisse reposer ces deux solutions pendant 3 heures, en les agitant de temps en temps, puis on ajuste au pH 4 par addition d'une solution d'acide citrique. Le volume est complété à 10 ml par addition d'eau distillée. On fait passer les solutions sur les colonnes

préalablement préparées. On rince le ballon jaugé et la partie supérieure de la colonne avec la solution tampon de pH 4 diluée 1/1, puis on lave plusieurs fois la colonne avec une solution de HCl 0.1 *M*. La B_{12} est fixée dans le haut de la colonne et on récupère la solution et les eaux de lavage au moyen de récipients jaugés de 10 ml placés au bas de la colonne. Le lavage est poursuivi jusqu'à ce que les eaux de lavage ne présentent plus de radioactivité. Dans ces conditions on peut estimer que la séparation est rigoureusement quantitative, à moins que des traces de cobalt ionique ne soient retenues irréversiblement sur la résine. Les résultats sont donnés dans le Tableau III.

TABLEAU III

SÉPARATION COBALT-60–VITAMINE B_{12}

	1ère Série		*2ème Série*	
	Solution A (avec B_{12})	*Solution B (sans B_{12})*	*Solution A (avec B_{12})*	*Solution B (sans B_{12})*
Activité initiale de la solution en c.p.m.	54317	54171	55517	56177
Activité des eaux de rinçage et lavage (élution de Co)				
1ère lavage (10 ml)	9547	9765	15369	16534
2ème lavage (10 ml)	40613	40289	37322	35950
3ème lavage (10 ml)	2575	2409	1523	2128
4ème lavage (10 ml)	208	321	439	530
5ème lavage (10 ml)	nulle	nulle	8	12
Activité non récupérée (en %)	−4%	−4%	−1.5%	−3%

On observe une perte d'ions cobalt qui peut aller jusqu'à 4 %. Si ces ions restent avec la B_{12}, il est évident que la méthode est inutilisable. Il fallait s'en assurer, aussi avons-nous, après élimination des ions cobalt et lavage prolongé des colonnes, élué la B_{12} par le dioxane. Nous l'avons dosé comme indiqué à la page 36. La valeur moyenne trouvée est 19.7 μg de B_{12} avec des variations de $\pm$ 1.5 % sur les 20 μg que contenaient les échantillons. D'infimes traces de cobalt sont donc fixées irréversiblement sur la résine, elles ne gênent pas le dosage.

Séparation vitamine B_{12} marquée–ions cobalt. Nous nous sommes assuré que la solution marquée de B_{12} (p. 31) ne renfermait pas d'impuretés radioactives, ce qui est le cas puisque le spectre gamma de ces échantillons ne montre que les pics du cobalt-60. Il fallait aussi être certain qu'il n'y avait pas, avec la B_{12}, des ions cobalt-60, même en très petites quantités. Nous avons effectué une séparation sur résine comme indiqué ci-dessus. La solution ne présentait, après passage sur la résine, aucune

TABLEAU IV

DISTRIBUTION DE LA B_{12} DANS LES DIVERSES FRACTIONS DE L'ÉLUAT

Diamètre de la colonne (mm)	*Volume de résine (ml)*	*Activité totale initiale (c.p.m.)*	*Activité des fractions de 2 ml de solution de dioxane (c.p.m.)*						*Total*
			1	*2*	*3*	*4*	*5*	*6*	
10	6	1813	1434	307	40	22	7	nulle	1810
10	6	1822	1822	326	41	25	nulle	nulle	1812
13	8	1834	1376	217	60	34	34	15	1721

radioactivité et ne contenait donc pas de cobalt-60. Par contre, après élution de la B_{12}, l'activité gamma totale fut retrouvée dans le dioxane.

Remarques. Les essais de séparation effectués sur des colonnes de 13 mm de diamètre donnent des pertes supérieures en B_{12}, de l'ordre de 6 à 10 %. Ces colonnes ne conviennent donc pas. D'autre part, pour déterminer le volume de dioxane minimum nécessaire à l'élution quantitative de la vitamine, les divers éluats ont été récupérés par fraction de 2 ml et l'activité de ceux-ci mesurée.

Comme on le voit, 10 ml d'éluat permettent d'extraire le totalité de la B_{12}. On peut en récupérer environ 97 % en 6 ml en prenant la précaution suivante: la surface de la résine doit être maintenue horizontale pendant toute l'opération, et il faut éviter d'agiter la résine lors de l'addition des diverses solutions. La colonne de 10 mm de diamètre donne de bons résultats. Enfin il ne faut ajouter le dioxane que lorsque la fraction précédente est complètement écoulée. Par la suite, nous avons diminué encore la quantité d'éluat nécessaire: avec 4 ml on récupère les 95 % de la B_{12}.

Sélectivité de la méthode. Le fer comme le cobalt joue un rôle important dans le traitement de l'anémie, et de ce fait, peut se trouver en grande quantité dans les produits pharmaceutiques renfermant de la B_{12}. Le rapport peut atteindre B_{12}:Fe = 1:5000 en poids et bien que la coloration due au N.S.R. soit sélective pour le cobalt en milieu nitrique, le fer en grandes quantités gêne le dosage par sa propre coloration. Des essais de séparation de solution renfermant des traces de B_{12} et des quantités d'ion cobalt et d'ion fer(II), ce dernier marqué au ^{59}Fe, ont montré qu'en procédant comme il est indiqué à la p. 34 le fer est quantitativement éliminé de la colonne, avec le cobalt.

Mode opératoire pour la séparation et le dosage de la vitamine B_{12}

Pour la mise au point définitive de ce dosage, nous nous sommes inspirés de l'étude analytique précédente. Nous avons employé des colonnes de 25 cm de hauteur et de 7 mm de diamètre et avons introduit environ 4 ml de résine, ce qui correspond à une hauteur dans la colonne de 7 mm; celle-ci est recouverte de quelques mm de laine de verre.

Dans ces conditions la détermination de la vitamine B_{12} est possible pour des quantités minimum de 5 μg de vitamine dans un volume final de 2.5 ml (2 μg/ml). On procède de la façon suivante:

L'échantillon contenant la vitamine B_{12} est dissous dans environ 10 ml du tampon pH 4 (v. p. 31) dilué 1:1 et la solution est introduite dans un bécher. Pour un dosage très précis dans lequel les pertes doivent être exactement déterminées, on ajoute 0.5 ml de la solution de vitamine B_{12} marquée au cobalt-60, dont l'activité est mesurée au moyen d'un compteur à scintillation.

On laisse écouler la solution obtenue à travers la colonne chromatographique à la vitesse d'environ 0.5 ml/min. On rince ensuite le bécher par 3 fois avec 5 ml du tampon pH dilué que l'on fait passer à travers la résine. La colonne est lavée avec 15 ml de HCl 0.1 *N*.

La vitamine est éluée au moyen de la solution de dioxane–chlorhydrique, 10 à 12 ml suffisent; on récupère les 6 premiers ml d'éluat contenant les 90 à 95 % de la vitamine B_{12} dans une capsule de verre et 4 ml seulement si on dispose d'un traceur. (Lorsque la quantité de B_{12} est supérieure à 20 μg on peut suivre l'élution par le déplacement le long de la colonne d'une bande rose.) Lorsqu'on a peu de vitamine en solution, il est possible de distinguer la différence de phase entre le HCl et le dioxane.

On ajoute à la capsule, 1 ml de la solution de NaCl (v. p. 31) et 1 ml d'acide nitrique

concentré. On évapore à sec sous une calotte chauffante afin de détruire les matières organiques provenant de la colonne.

On reprend le résidu 2 fois par 0.5 ml d'acide perchlorique et on évapore chaque fois à siccité aux rayons I.R. On reprend le résidu, qui doit être tout à fait blanc, par quelques ml d'eau bidistillée et on évapore à nouveau pour chasser les dernières traces d'acide. Après refroidissement, on reprend le résidu par 3 fois 1 ml de la solution tampon pH 6. Ces solutions sont versées dans un ballon jaugé de 5 ml.

On ajoute à la solution précédente 1 ml de la solution de N.S.R. La solution est chauffée 1 min au bain marie. Après adjonction de 1 ml d'acide nitrique concentré on continue à chauffer pendant 60 sec. Après refroidissements sous courant d'eau, on complète à 5 ml par de l'eau bidistillée.

On introduit la solution dans une macrocuve (long. 10 mm $\pm$0.01; vol. 1 à 3 ml). La densité optique est mesurée au spectrophotomètre Beckman à la longueur d'onde de 520 mμ, par rapport à un blanc préparé de la même façon mais sans vitamine.

Dans le cas où l'on a introduit un indicateur de perte, l'activité est déterminée sur 2 ml de la solution finale (complexée au N.S.R.) au compteur à scintillation et on détermine le facteur de pertes par lequel il faudra multiplier les résultats obtenus.

Remarque. Les opérations de contrôle ont été déjà indiquées à la page 33.

La détermination colorimétrique de la teneur de la vitamine B_{12} peut être faite de deux manières:

(1) *Par courbe d'étalonnage.* Pour le calcul des résultats on peut se référer à la courbe d'étalonnage (v. p. 33, Tableau I).

Le tableau ci-dessous montre la nécessité, quand on travaille sans traceur, de récupérer au moins 6 ml de l'éluat de dioxane et de déterminer un facteur correctif. Facteur d'activité: coefficient de pertes obtenu par les mesures d'activité avant et après l'expérience.

TABLEAU V

RÉSULTATS DES DOSAGES EFFECTUÉS

(a) *Avec traceur*						
Prise initiale de vit. B_{12} en μg	10	20	20	30	40	50
Vol. final du complexe en ml	2.5	5	2.5	5	5	5
Nombre d'essais	6	10	6	6	6	6
Valeur moy. trouvée en μg (sur 4 ml d'éluat)	9.85	17	18	27	34.6	42
Erreur %	−1.5	−15	−10	−10	−13.5	−16
Valeur corrigé par le facteur d'activité	10.6	19.29	19.63	30.37	39.1	49
Erreur %	+6	−3.55	−1.7	+1.3	−2.4	−2
(b) *Sans traceur*						
Valeur moy. trouvée en μg (sur 6 ml d'éluat)	9.85	18.3	18.8	29.2	38.2	48
Erreur %	−1.5	−8.5	−6	−2.4	−4.5	−4

Facteur correctif: coefficient obtenu d'après l'erreur relatif dans une série d'expérience lorsqu'on n'emploie pas de traceurs.

(2) *Méthode par étalon interne.* Il est souvent préférable d'utiliser la méthode par étalon interne. Dans ces conditions on procédera comme indiqué ci-dessus avec les modifications suivantes: une solution renferme la quantité inconnue x; une seconde

renferme la quantité x plus une quantité connue de vitamine B_{12}. Les séparations et le dosage se ferront comme précédemment. Les résultats sont donnés dans le Tableau VI.

TABLEAU VI

DOSAGE PAR ÉTALON INTERNE AVEC ET SANS TRACEUR

Prises x μg B_{12}	*Etalon interne* μg B_{12}	*Valeurs trouvées pour x*			
		Avec traceur	*Erreur %*	*Sans traceur*	*Erreur %*
10	20	10.45	4.5	8.5	15
10	10	10.65	6.5	8.8	12
20	20	19.6	2	18.7	8.5
25	25	25.9	3.6	22.8	8.8
5	5	5.2	4	4.66	6.8
5	5	4.8	4	4.16	16.8
20	10	18.8	6	17.3	13.5

APPLICATION AU DOSAGE DE LA VITAMINE B_{12} DANS LES PRODUITS PHARMACEUTIQUES

Nous avons déterminé la vitamine B_{12} dans divers produits pharmaceutiques par la méthode décrite plus haut. On prélève une quantité d'échantillons telle qu'il y ait au moins 5 μg de B_{12}. Si l'échantillon est solide (tablettes, pastilles . . .) on le dissout dans l'eau et on sépare la phase insoluble par centrifugations et lavages répétés. A chaque prise on y ajoute une quantité connue de vitamine B_{12}, marquée au cobalt-60 et on mesure l'activité au moyen d'un compteur à scintillation. Dans le cas d'un échantillon solide on introduit le traceur après la mise en solution et avant la centrifugation.

Le mode opératoire est donné à la page 36, néanmoins il est nécessaire de le modifier quelque peu selon les substances qui accompagnent la vitamine B_{12}.

Dosage de la B_{12} en présence de substances liposolubles. Pour que la méthode précedente de séparation de la vitamine B_{12} soit utilisable l'échantillon ne doit pas renfermer des substances liposolubles, tel que les vitamines A, D, E et K, qui perturbent le dosage par leur coloration. En effet elles sont souvent en grande quantité, environ 0.5 mg de vitamine A pour 0.5 μg de B_{12}. Elles restent adsorbés en haut de la colonne de résine et sont éluées par le dioxane avec la vitamine B_{12}. La séparation s'effectue en éluant ces vitamines fixées sur la résine par 15 ml d'acétone après le lavage de la colonne par 15 ml de solution HCl 0.1 *N*; toutes les impuretés liposolubles sont ainsi éliminées. On peut suivre l'élution des vitamines par le déplacement d'une bande colorée sur la colonne. On lave à nouveau avec 7 ml de HCl 0.1 *N* avant d'éluer la vitamine B_{12} avec le dioxane.

Nous avons vérifié l'effet du passage de la solution d'acétone sur la vitamine B_{12} (qui est insoluble dans ce solvant), en ajoutant à une solution de vitamines A et D une quantité de vitamine B_{12} marquée au cobalt-60, d'activité connue. Après lavage, séparation à l'acétone et élution de la vitamine au moyen du dioxane–HCl, l'activité est de nouveau déterminée.

On peut constater que la vitamine B_{12} adsorbée sur la résine, n'est pas éluée par le passage de 15 ml d'acétone.

Dosage de la vitamine B_{12} en présence d'un complexant. La vitamine B_{12} se trouve parfois dans certains produits sous forme d'extrait de foie ou combinée avec des protéines ou des peptides, car la combinaison vitamine B_{12}–facteur intrinsèque (qui est administrée par voie buccale) est plus active que la vitamine B_{12} libre dans les traitements

de l'anémie pernicieuse. Il est préférable de libérer la vitamine B_{12} de ce complexe avant de procéder aux opérations de séparation et de dosage[14]; afin d'y parvenir on met la solution de l'échantillon en contact avec du cyanure (2 ml d'une solution de KCN 10 %). On porte la solution au pH 7.5 par addition d'acide citrique et on maintient le tout pendant 3 à 4 heures à la température environnante, ou pendant 30 min à 60°, puis on procède comme il est indiqué à la page 36.

Exemples des produits pharmaceutiques dosés. Nous avons effectué le dosage de la vitamine B_{12} sur les produits suivants.

(1) *Calcium 4* (Sauter).

Composition: Vit. B_{12} 2 μg; vit. A 1000 U.I.; vit. D 750 U.I.; vit. C 0.04 g; phosphate, gluconate et lactate de Ca.

Résultat du dosage: 1.9 $\pm$ 0.1 μg de vit. B_{12}/capsule.

(2) *Glutadouze.*

Composition: Extrait de foie titrant en B_{12} 10 μg.
Extrait d'antre pylorique correspondant à 10 g d'organe f.
Extrait de rate correspondant à 10 g d'organe f.
Extrait cérébro médullaire correspondant à 5 g d'organe f.
Glycérophosphate Na 0.5 g; glutamate Na 0.4 g.

Résultat du dosage: 9.7 $\pm$ 0.5 μg de vit. B_{12}.

(3) *Hemofer* (Vifor).

Composition: Les fumarates ferreux (245 mg), de Co (3.5 mg) et de Mn (0.17 mg). Vit. B_{12} 4 μg; vit. C 100 mg; sorbitol 25 mg.

Résultat du dosage: 4.17 $\pm$ 0.25 μg de B_{12}/comprimé.

(4) *Bejectal-C* (Abbott).

Composition: Par ml — Vit. B_1 20 mg, B_2 3 mg, B_{12} 2 μg, B_6 5 mg; nicotinamide 75 mg; acide pantothénique 5 mg; vit. C 100 mg.

Résultat du dosage: 1.95 $\pm$ 0.1 μg de vit. B_{12}/ml.

(5) *Gerioptil* plus H_3.

Composition: Par capsule — Diméthyl aminoéthanol glutamate 10 mg; ac. *p*-amino-benzoique 10 mg; vit. A 2500 U.I.; vit. B_1 2 mg, B_{12} 1 μg, B_6 0.5 mg; vit. C 50 mg; ac. folique 0.2 mg; vit. E 3.5 mg; adénosine 1 mg; ac. gras non saturés 50 mg; rutin 10 mg; traces de Mn, Mg, Ca, Zn, Fe/SO_4, etc.

Résultat du dosage: 0.92 $\pm$ 0.1 μg de vit. B_{12}/capsule.

(6) *Vi-Daylin* (Abbott).

Composition: Par 5 ml — Vit. A 3000 U.I.; vit. D 800 U.I.; vit. B_{12} 3 μg; thiamine 1.5 mg; riboflavine 1.2 mg; vit. C 40 mg; nicotinamide 10 mg.

Résultat du dosage: 3.1 $\pm$ 0.15 μg de vit. B_{12}/5 ml.

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RÉSUMÉ

Il est proposé un dosage indirect de traces de vitamine B_{12}. Celle-ci est décomposée et le cobalt libéré est déterminé colorimétriquement par le nitroso-sel R. Cette méthode permet de doser 5 à 10 μg de B_{12}. L'emploi d'un traceur (B_{12} marquée au cobalt-60) et d'un étalon interne donne une grande précision à la méthode dont l'erreur dans ces conditions ne dépasse pas 6%.

Au moyen d'une résine échangeur d'ions, il est possible d'éliminer toute trace de cobalt ionique avant la déstruction de la B_{12}. La méthode présente une grande sensibilité et une bonne sélectivité, seuls les homologues de la B_{12} renfermant du cobalt gênent le dosage. La B_{12} a été dosée dans de nombreux produits pharmaceutiques. Selon les substances qui l'accompagnent, un traitement approprié très simple est nécessaire.

SUMMARY

An indirect determination of traces of vitamin B_{12} is proposed; the vitamin is decomposed and the liberated cobalt is determined colorimetrically with Nitroso-R salt. 5–10 μg of B_{12} can be determined. The use of tracers and internal standards decreases the error to less than 6%. Before the decomposition of the B_{12} all traces of ionic cobalt are removed by means of an ion-exchange resin. The method is very sensitive and fairly selective; only homologues of B_{12} containing cobalt interfere. B_{12} can be determined in many pharmaceutical products.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Vitamin B_{12}. Sie beruht auf der colorimetrischen Bestimmung des Kobalts mit Nitroso-R-Salz nach Zerstörung der organischen Substanz. Kobalt, das nicht an B_{12} gebunden ist, wird vorher mit Hilfe eines Austauscherharzes entfernt.

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DETERMINATION OF ZIRCONIUM AND HAFNIUM WITH XYLENOL ORANGE AND METHYLTHYMOL BLUE*

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Xylenol Orange, [3,3'-bis-N,N-di(carboxymethyl)-aminomethyl]-*o*-cresolsulphonphthalein, and Methylthymol Blue, [3,3'-bis-N,N-di(carboxymethyl)aminomethyl]-thymol-sulphonphthalein, were first introduced by KÖRBL AND PŘIBIL[1] as metal indicators for the ethylenediaminetetraacetic acid (EDTA) titration, and the lower pH limit with respect to the cation reactions with Xylenol Orange was also reported. Xylenol Orange has been used as a chromogenic agent for the determination of traces of highly charged metal ions such as zirconium(IV) and hafnium(IV) and bismuth(III) and iron(III) in a strongly acidic medium, and shows highly selective reactions with these cations[2-4]. Methylthymol Blue has not been previously reported as a chromogenic agent for the determination of metals.

Since the two reagents are similar in structure, it is interesting to compare their chemical properties and reactions with highly charged metal ions in an acidic medium. In this paper their reactions and analytical applications for the determination of zirconium and hafnium are reported in detail. The formation constant of the zirconium complex of Methylthymol Blue has been determined. Zirconium forms an intensely colored complex with Xylenol Orange or Methylthymol Blue in a strongly acidic medium (0.8–1.0 *N*). In contrast, hafnium requires a pH of 3 with Methylthymol Blue and an acidity of 0.2 *N* (perchloric acid) with Xylenol Orange for maximum color development. The masking effect of hydrogen peroxide on the color development of the Xylenol Orange complexes of zirconium and hafnium has been previously described[3]. Additional findings on this peroxide masking and the use of sulfate in the determination of hafnium in the presence of zirconium are now given. In the past, there has been no direct chemical method for the determination of zirconium or hafnium in the presence of each other, that is, without prior separation. The present investigation demonstrates such a possibility through a masking and demasking approach.

The structures and the acid dissociation constants of the two dyes have been reported[5,6].

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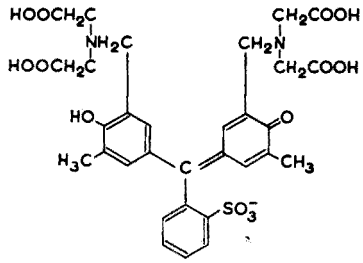
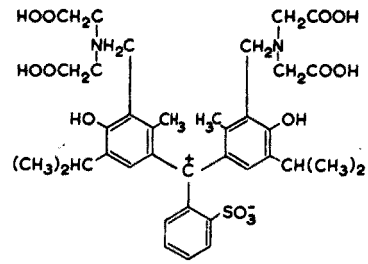


(I) Xylenol Orange



(II) Methylthymol Blue

Both Xylenol Orange and Methylthymol Blue are aminopolycarboxylic acids, as is EDTA, with two coordinating centers, but they form weaker complexes with cations than EDTA. However, they still form relatively strong complexes with the highly charged cations in a strongly acidic medium (see Table I).

TABLE I

METALS GIVING COLOR REACTIONS WITH XYLENOL ORANGE AND METHYLTHYMOL BLUE IN ACIDIC MEDIUM (0.1–0.2 N $HClO_4$)[a]

Metal	*Xylenol Orange*	*Methylthymol Blue*	*Masked by*
Bismuth	red	red-violet	chloride
Iron(III)	purplish red	blue	ascorbic acid
Tin(IV)	red (heat)	red (heat)	fluoride
Zirconium	red	red	fluoride, H_2O_2
Hafnium	red	red	fluoride
Thorium	red	red	fluoride
Niobium	red (heat)	red (heat)	fluoride
Molybdenum(VI)	reddish (heat)	red (heat)	H_2O_2
Vanadium(IV)	reddish	reddish	
Titanium(IV)	red	violet blue	fluoride

[a] Cerium(IV) oxidizes the dyes; Se(IV), Te(IV), Pt(IV), Ge, Ta, W, and other cations do not give color reactions with the dyes at the studied acidity. EDTA masks all the above-mentioned metals including niobium (partially masked).

EXPERIMENTAL

Apparatus and reagents

Standard zirconium solution ($1.0 \cdot 10^{-3}$ M). Prepared from pure zirconium metal which was dissolved in 1 : 1 nitric acid and the minimum amount of hydrofluoric acid followed by fuming with perchloric acid, and diluted with water and dilute perchloric acid to a known value such that its solution was 1.0 N in perchloric acid. More dilute solutions were prepared from this stock solution by appropriate dilution with water.

Standard hafnium solution ($1.0 \cdot 10^{-3}$ M). Prepared in the same manner as the standard zirconium solution from pure hafnium oxide containing 60 p.p.m. zirconium (obtained from Wah Chang Corporation). It was noted that in the dissolution of the hafnium oxide, hafnium perchlorate crystallized upon fuming with perchloric acid, suggesting that hafnium perchlorate is slightly soluble and that zirconium perchlorate is more soluble in concentrated perchloric acid.

Xylenol Orange solution. $1.0 \cdot 10^{-3}$ *M* and $5.0 \cdot 10^{-4}$ *M* solutions were prepared from the product of Chemapol of Prague.

Methylthymol Blue solution. $1.0 \cdot 10^{-3}$ *M* and $5.0 \cdot 10^{-4}$ *M* solutions were prepared from the product of Distillation Products Industries of Rochester.

Formic acid. Prepared by diluting 90% formic acid with an equal volume of water.

Other reagents were analytical grade. A Beckman Spectrophotometer, Model DU, with 1-cm absorption cells, and a Beckman pH meter, Model M, or equivalent were used.

Absorption spectra

Both Xylenol Orange and Methylthymol Blue are acid-base indicators, undergoing a color transition from yellow to purple or red at pH 6 to 7. Their solutions are pink to red in 1 : 1 sulfuric acid or concentrated perchloric acid. The yellow solutions of the dyes show a maximum absorption at approximately 440 mμ; the red Xylenol Orange complexes of zirconium and hafnium show maximum absorption at 535 mμ and 530 mμ respectively, and the red Methylthymol Blue complexes of zirconium and hafnium at 580 mμ and 570 mμ respectively. With Methylthymol Blue, when either zirconium or hafnium is in excess, a violet complex is formed showing a maximum absorption at 595 to 600 mμ. The absorption spectra of the dyes and their zirconium and hafnium complexes are shown in Fig. 1.

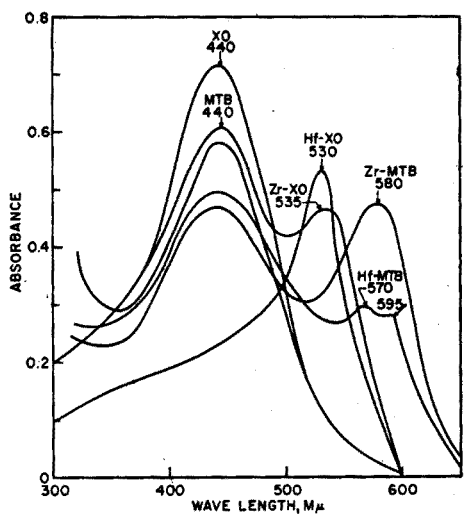


Fig. 1. Absorption spectra.

Calibration curves

(1) Zirconium with Methylthymol Blue. Pipet 1.0–5.0 ml aliquots of a $1.0 \cdot 10^{-4}$ *M* zirconium solution into a 25-ml volumetric flask. Add 5.0 ml of 5.0 *N* perchloric acid and 1.0 ml of $1.0 \cdot 10^{-3}$ *M* Methylthymol Blue solution. Dilute to the mark with water and mix. After 45 min, measure the absorbance at 580 mμ against a reagent blank. Beer's law is followed.

(2) Hafnium with Methylthymol Blue. Pipet 1.0–5.0 ml aliquots of a $1.0 \cdot 10^{-4}$ *M*

hafnium solution into a 100-ml beaker. Add 1 ml of 1 : 1 formic acid and 1.0 ml of $1.0 \cdot 10^{-4}$ *M* Methylthymol Blue solution, dilute to approximately 15 ml with water, and adjust to pH 3.0 $\pm$ 0.2 with dilute hydrochloric acid or ammonium hydroxide. Transfer to a 25-ml volumetric flask and dilute to the mark with water. After 5 min, measure the absorbance at 570 mμ against a reagent blank. A straight line is obtained, but sometimes it may not go through the origin.

(3) Zirconium and hafnium with Xylenol Orange. The procedures for establishing these calibration curves have been previously described[2,3]. All the calibration curves are shown in Figs. 2 and 3.

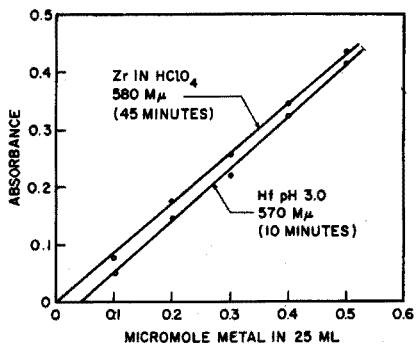


Fig. 2. Calibration curves with Methylthymol Blue.

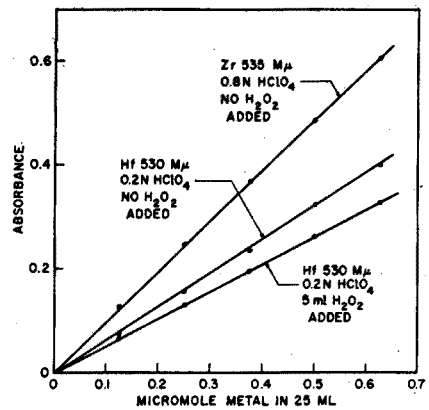


Fig. 3. Calibration curves with Xylenol Orange.

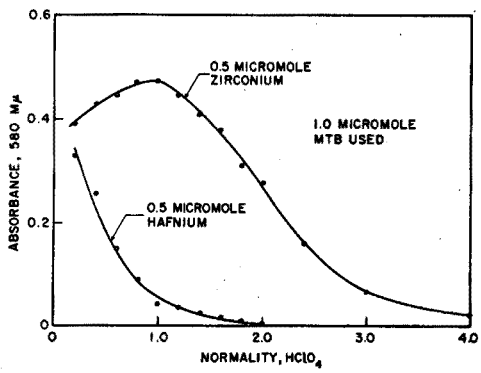


Fig. 4. Effect of acidity on Methylthymol Blue complexes of zirconium and hafnium.

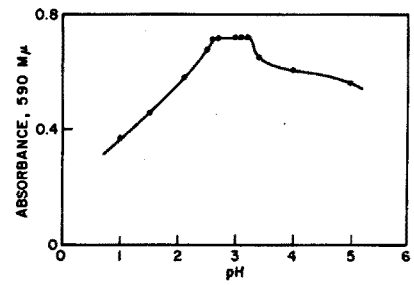


Fig. 5. Effect of pH on color development of hafnium–Methylthymol Blue complex.

DISCUSSION

Effect of acid

The effect of different acids and their quantities on the color development of Xylenol Orange complexes of zirconium and hafnium has been previously reported. The optimum acidities for their maximum color development with perchloric acid are given in Table II.

TABLE II

SOME PROPERTIES OF THE ZIRCONIUM AND HAFNIUM COMPLEXES OF XYLENOL ORANGE AND METHYLTHYMOL BLUE[a]

	Xylenol Orange $pk_1 = 2.6$, $pk_2 = 3.2$, $pk_3 = 6.4$, $pk_4 = 10.5$, $pk_5 = 12.3$		Methylthymol Blue $pk_{1-3} = 4.5$, $pk_4 = 7.2$, $pk_5 = 11.2$, $pk_6 = 13.4$	
	Zirconium	*Hafnium*	*Zirconium*	*Hafnium*
λ max, mμ	535 —	530 —	580 (600)	570 (590)
Optimum color development	0.5–1.0 *N* $HClO_4$	0.2–0.4 *N* $HClO_4$	0.3–1.2 *N* $HClO_4$	0.001 *N* (pH 3)
Formation constant (*K*) (1 : 1 complex)	$4.0 \cdot 10^7$ (0.8 *N* $HClO_4$)	$3.2 \cdot 10^6$ (0.3 *N* $HClO_4$)	$1.0 \cdot 10^5$ (1.0 *N* $HClO_4$)	
Molar absorptivity	24,200 (0.8 *N* $HClO_4$)	15,700 (0.2 *N* $HClO_4$)	21,700 (1.0 *N* $HClO_4$)	18,700 (pH 3)
Sensitivity (log I_0/I = 0.001), $\mu g/cm^2$	0.004	0.011	0.004	0.010
Colored complex	red	red	red (1 : 1) violet (2 : 1)	red (1 : 1) violet (2 : 1)
Masked by	EDTA, F^- citrate H_2O_2 phosphate	EDTA, F^- citrate phosphate	EDTA, F^- citrate H_2O_2 phosphate	EDTA, F^- citrate phosphate

[a] The acid dissociation constants of the two dyes are available in the literature [5,6].

The color of the zirconium complex of Methylthymol Blue can be developed over a wide range of acidity; with perchloric acid the range 0.8 to 1.0 *N* is optimum, as is also the case with the zirconium complex of Xylenol Orange. The hafnium complex of Methylthymol Blue shows its maximum color development at about pH 3, in contrast to the hafnium complex of Xylenol Orange which shows maximum color development at about 0.2–0.3 *N* perchloric acid (see Figs. 4 and 5). Other acids, such as hydrochloric and sulfuric, have been studied in the color development of the Xylenol Orange complexes of zirconium and hafnium; however, only perchloric acid was used in the present investigation of the Methylthymol Blue complexes of zirconium and hafnium.

Stability

The zirconium and hafnium complexes of the two dyes are stable for at least 24 h. The aqueous solutions of the two dyes are stable for at least a few days but show decomposition after a few months. It was found that the Methylthymol Blue solution is less stable than the Xylenol Orange solution. The hafnium complexes of Xylenol Orange and Methylthymol Blue are decolorized overnight when hydrogen peroxide is present.

Effect of time on color development

The color reactions of Xylenol Orange with zirconium and hafnium are almost instantaneous, but for maximum color development the zirconium complex of Methylthymol Blue requires a standing period of 45 min (see Fig. 6).

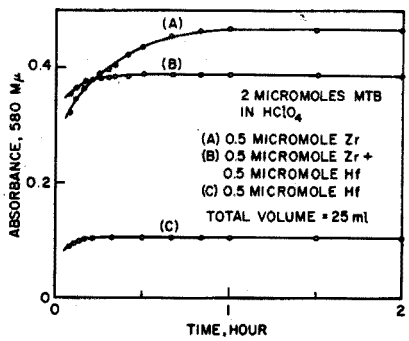


Fig. 6. Effect of time.

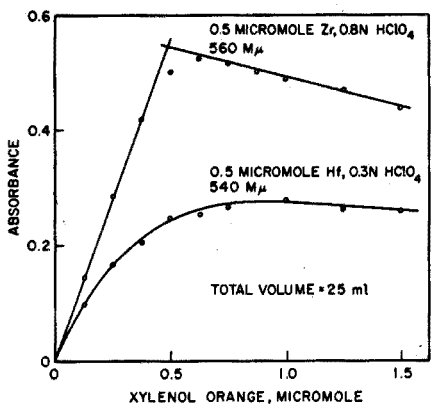


Fig. 7. Effect of Xylenol Orange.

Sensitivity

Both Xylenol Orange and Methylthymol Blue are sensitive reagents for zirconium and hafnium. The molar absorptivity and sensitivity of the dye complexes are listed in Table II. It is to be noted that the two dyes are slightly more sensitive to zirconium than to hafnium and that Xylenol Orange is more sensitive to both metals. In Figs. 2 and 3, the curves show that Methylthymol Blue is more sensitive to hafnium than Xylenol Orange, but maximum color development occurs at different acidities. If the color of the hafnium complex of Methylthymol Blue is developed in 0.2 or 0.3 *N* perchloric acid, its sensitivity is much less than that of Xylenol Orange at this acidity.

Selectivity

As shown in Table I, the two dyes in a rather acidic medium react with only the highly charged metal ions. The selectivity of Xylenol Orange for zirconium is about the same as Methylthymol Blue as they both form colored complexes with zirconium at an acidity of 0.8 to 1.0 *N* (perchloric acid). The selectivity of Methylthymol Blue for hafnium is not as high as that of Xylenol Orange since the formation of the colored hafnium complex of Methylthymol Blue requires a much lower acidity at which many other metals ions also react with the dye. The use of certain masking agents, such as ascorbic acid for iron(III) and chloride for bismuth, can further increase the selectivity of the dyes to zirconium and hafnium. The use of hydrogen peroxide as a masking agent in the determination of hafnium in the presence of zirconium will be discussed later.

Effect of reagent concentration

For 0.5 micromole of zirconium in 0.8 *N* perchloric acid, from 0.5 to 1.0 micromole of Xylenol Orange is sufficient for full color development; the absorbance decreases

with larger amounts of the dye as shown in Fig. 7. For 0.5 micromole of hafnium, from 0.7 to 1.5 micromoles of Xylenol Orange is sufficient; no significant decrease in absorbance occurs with larger amounts of the dye. For 0.5 micromole of zirconium, 1.0 to 3.0 micromoles of Methylthymol Blue give constant absorbance; for 0.5 micromole of hafnium (at pH 3.0), maximum color development occurs at 1.0 micromole of Methylthymol Blue and the absorbance decreases with larger amounts of the dye as shown in Fig. 8. Such decrease in absorbance may be due to the formation of other species when the dye is in great excess. The different effect on absorbance of an excess of the two dyes on zirconium and hafnium should be noted and compared (Figs. 7 and 8). It may also be noted that when zirconium or hafnium is present in excess, a violet color, rather than red, is developed with Methylthymol Blue, but not with Xylenol Orange.

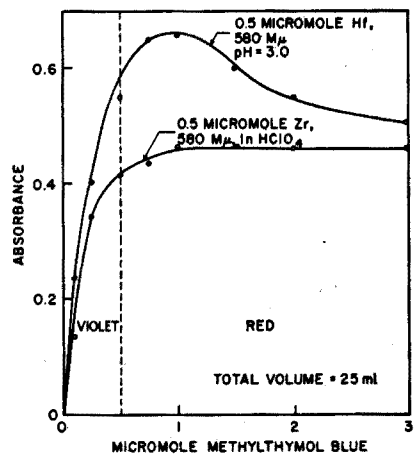


Fig. 8. Effect of Methylthymol Blue.

Effect of anion

EDTA, citrate, phosphate, and fluoride bleach the zirconium or hafnium complexes of the two dyes. More than 2 micromoles of sulfate begins to decrease the absorbance of 35 μg of zirconium in the Xylenol Orange procedure. With hafnium more sulfate can be tolerated. Perchlorate, chloride, and nitrate show no interference.

Complex formation

As reported previously (see also Fig. 7), Xylenol Orange forms predominantly a 1 : 1 complex with zirconium or hafnium when the dye is not present in too great an excess. Methylthymol Blue forms two colored complexes (red and violet) with either zirconium or hafnium, depending on whether the dye or the metal ion is present in excess, as mentioned above. Experiments were conducted to determine the molar ratio of the complexes by adding various amounts of zirconium to a constant amount of Methylthymol Blue and by adding various amounts of Methylthymol Blue to a constant amount of zirconium. The results shown in Figs. 9 and 10 indicate that when the dye is in excess, a 1 : 1 complex is formed and that when zir-

conium is in excess, a 2 : 1 zirconium–dye complex is formed. The existence of these complexes is also confirmed by the Job plots (Fig. 11).

Methylthymol Blue forms a 1 : 2 hafnium–dye complex at pH 3. With increasing acidity, a 1 : 1 complex is found to an increasing extent as shown in Fig. 12. It has been reported that Methylthymol Blue forms differently colored complexes with lead

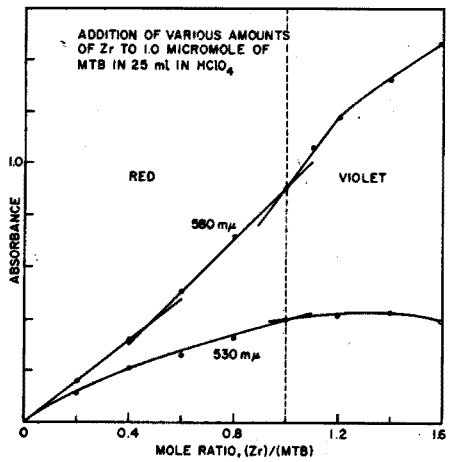


Fig. 9. Mole ratio — I.

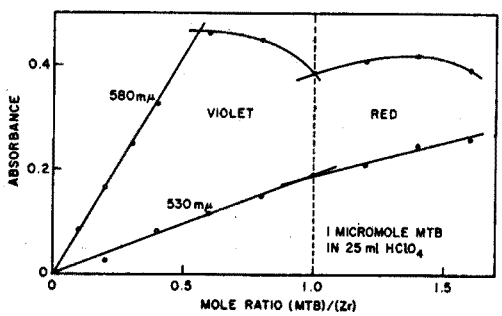


Fig. 10. Mole ratio — II.

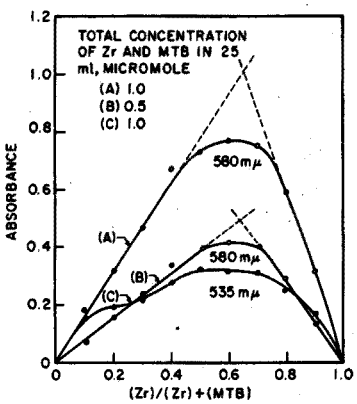


Fig. 11. Job curve for zirconium–Methylthymol Blue complex.

in a weakly acidic medium[7]. It is believed that whenever this dye is in excess, it also forms a 1 : 2 metal–dye complex in a weakly acidic medium (pH 3–6.5). That Methylthymol Blue can form violet 2 : 1 complexes with zirconium and hafnium, and not Xylenol Orange, may be attributed to the fact that one of the two phenolic hydrogens in Methylthymol Blue is more labile than that in Xylenol Orange. (see Formulas I and II).

The isopropyl groups in the structure of Methylthymol Blue as contrasted with methyl in Xylenol Orange, with the attendant steric effects, may explain why the former dye does not form a strong complex with hafnium in a rather acidic medium.

The linear relationship shown in Fig. 9 between the concentrations of zirconium and Methylthymol Blue, when the latter is in excess (molar ratio < 1) permits calculation of the formation constant of the 1 : 1 zirconium–Methylthymol Blue complex from the data represented by the left side of the curves in Fig. 11. It was found to be $1.0 \cdot 10^5$ in 1.0 N perchloric acid. This value also indicates that Methylthymol Blue forms a weaker complex with zirconium than Xylenol Orange, which has been found to have a formation constant of $4.0 \cdot 10^7$ at this acidity. In general, the stronger a complex is, the higher the acidity at which it can maintain itself. The relationship between the formation constant of the polyvalent metal complexes of Xylenol Orange and the lowest acidity at which maximum color development occurs is shown in Fig. 13.

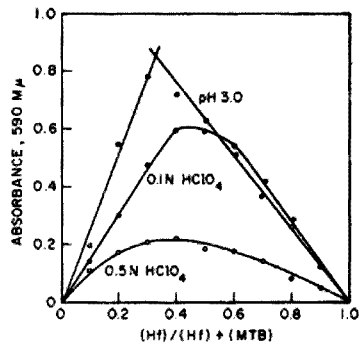


Fig. 12. Job curve for hafnium–Methylthymol Blue complex.

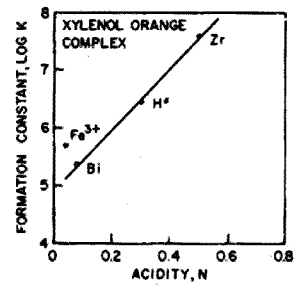


Fig. 13. Correlation of minimum acidity required for optimum complex formation and formation constant.

Determination of hafnium in presence of zirconium (employing Xylenol Orange and hydrogen peroxide masking)

The masking action of hydrogen peroxide on the formation of the zirconium complex of Xylenol Orange has been described[3]. Hydrogen peroxide also masks slightly the hafnium complex of Xylenol Orange in 0.2–0.3 N perchloric acid medium

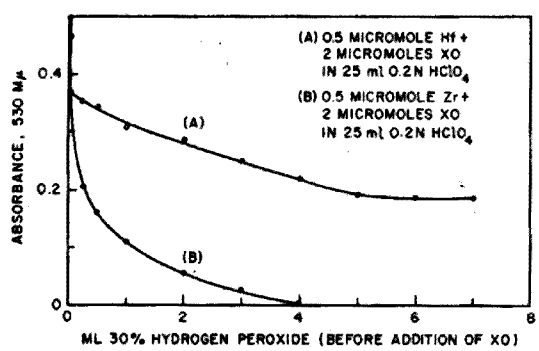


Fig. 14. Effect of hydrogen peroxide on color development of Xylenol Orange complexes of zirconium and hafnium

(Fig. 14). It will be seen that for 0.5 micromole of hafnium, the effect of the peroxide concentration is linear below 5 ml of 30% hydrogen peroxide; the addition of further peroxide does not show any significant effect. Furthermore, although the calibration curve for hafnium with addition of hydrogen peroxide is less sensitive than that obtained without peroxide, Beer's law is followed (Fig. 3). The lower curve in Fig. 15 shows that the presence of zirconium with hydrogen peroxide decreases the absorbance of the hafnium complex of Xylenol Orange and suggests that formation of a mixed peroxide complex of zirconium and hafnium may be involved. The upper curve shows an increase in the absorbance in the absence of hydrogen peroxide as zirconium is added. This can be explained as an additive effect caused by the formation of the red zirconium complex of Xylenol Orange. Since sulfate also complexes both zirconium and hafnium, an attempt was made to eliminate the formation of the assumed mixed peroxide complex. To 0.5 micromole of hafnium, 1.0 ml of 5 N perchloric acid, and various amounts of zirconium were added, followed by 5.0 ml of 30% hydrogen peroxide, 1.0 millimole of sodium sulfate and 2 ml of $1.0 \cdot 10^{-3}$ M Xylenol Orange solution. The total volume was brought to 25 ml with water. The results are shown by the middle curve of Fig. 15, and indicate that hafnium can be determined in the presence of zirconium. Here, we may consider that hydrogen peroxide masks the zirconium interference and that sulfate acts in a demasking sense by eliminating the effect of hydrogen peroxide on hafnium when zirconium is also present. For the analysis of a mixture of zirconium and hafnium, the total absorbance of the Xylenol Orange

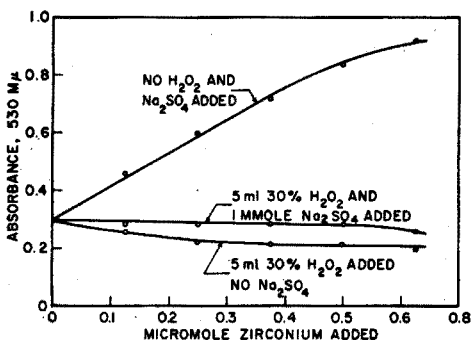


Fig. 15. Determination of hafnium in presence of zirconium using hydrogen peroxide as masking agent. 0.5 Micromole hafnium and 2 micromoles Xylenol Orange in 25 ml 0.2 N $HClO_4$.

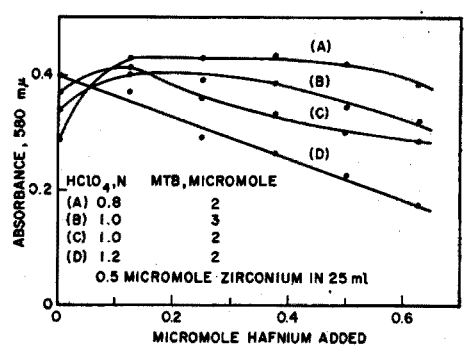


Fig. 16. Effect of hafnium on color of zirconium–Methylthymol Blue complex at different acidity.

complexes of both zirconium and hafnium is determined without addition of either hydrogen peroxide or sulfate, then the absorbance for hafnium alone is determined in a second aliquot by addition of both peroxide and sulfate. The difference represents the absorbance for zirconium. The determination of zirconium and hafnium in the presence of each other is a classical analytical problem. It appears that the use of masking and demasking actions represents a more effective approach than the synthesis of a highly selective organic reagent for zirconium or alternatively for hafnium.

Further photometric studies (use of Methylthymol Blue at high acidity)

The results in Fig. 4 indicate a possibility of determining zirconium in the presence of hafnium in a > 0.8 *N* perchloric acid medium, where hafnium is much less sensitive to Methylthymol Blue. But the results shown in Fig. 16 indicate little success by this approach. The use of higher acidity was studied. The results shown in Fig. 17 indicate that traces of hafnium have an apparent bleaching effect on the color of the zirconium complex of Methylthymol Blue in 2.4 *N* perchloric acid medium; in other words, hafnium reacts either with a zirconium ion or with the zirconium complex of Methyl-

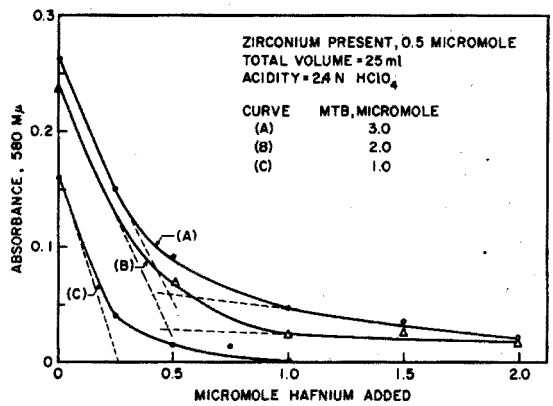


Fig. 17. Effect of hafnium on color of zirconium–Methylthymol Blue complex in 2.4 *N* perchloric acid medium.

thymol Blue existing at such high acidity. It should be emphasized that hafnium alone gives no color with this dye at this high acidity. Addition of sulfate or heating does not eliminate the bleaching effect of hafnium. Addition of more than 1 micromole of Methylthymol Blue for 0.5 micromole of zirconium increases the color intensity, as increasing amounts of hafnium are added, but does not change the bleaching phenomenon. Extrapolation of the Curves A and B indicates that 0.5 micromole of hafnium is used in a bleaching reaction with 0.5 micromole of zirconium. Extrapolation of Curve C shows the intersection at 0.25 micromole of hafnium, suggesting that an insufficient amount of Methylthymol Blue was present. It appears that two micromoles of Methylthymol Blue are required for 0.5 micromole of zirconium, that is, a 4 : 1 molar ratio. When the solution contained 0.5 micromole of zirconium and 1.0 micromole of Methylthymol Blue, only 0.25 micromole of the zirconium complex of Methylthymol Blue was formed, therefore, also only 0.25 micromole of hafnium was required for reacting with the zirconium complex of Methylthymol Blue as shown by Curve C. So the reaction ratio of zirconium to hafnium was 1 : 1 in this case. A similar bleaching reaction was also observed when zirconium was added to the hafnium complex of Methylthymol Blue at pH 2–3; this may be regarded as the bleaching effect of zirconium. This bleaching reaction of hafnium is obviously a complicated one and deserves further study. From the analytical point of view, a quantitative relationship is seen between zirconium, hafnium, and the dye, and this relationship may be utilized to develop methods of determining either of the two metals or the dye.

It may be recalled that bleaching of a colored zirconium complex with fluoride has long been used for the microdetermination of fluoride and of zirconium. The present bleaching reaction of hafnium may be compared to that of fluoride, but with the advantage of a 1 : 1 reaction.

Zirconium in the presence of an excess of Methylthymol Blue may also be titrated photometrically with a hafnium or dye solution (Fig. 17).

The following observations may help towards an understanding of the nature of the bleaching reaction of hafnium. It was noted that regardless of the order in which hafnium or Methylthymol Blue is added to the zirconium solution, the hafnium bleaching reaction is the same. It was also noted that the same bleaching effect was observed in a 2.4 *N* hydrochloric acid medium suggesting that the acid anion is not primarily involved in the bleaching reaction. Addition of an excess amount of hafnium to the zirconium complex of Methylthymol Blue did not decrease the absorbance of the dye (440 mμ), suggesting that hafnium seems to have no reaction with the dye at this high acidity. Methylthymol Blue shows an absorption maximum at 275 mμ in a 2.4 *N* perchloric acid medium; both the zirconium and hafnium complexes of the dye show no additional absorption maximum other than 275 mμ in the ultraviolet region, suggesting that there is probably no hafnium–Methylthymol Blue complex formed at this high acidity. And although Xylenol Orange does not form an intensely colored complex with either zirconium or hafnium in a 2.4 *N* perchloric acid medium, the hafnium bleaching reaction was also observed with this dye.

Based on this limited information, three possible interpretations might be considered: (*1*) a displacement reaction in which hafnium displaces zirconium from the dye complex forming a colorless or a less intensely colored complex itself with the dye; (*2*) the formation of a colorless or less intensely colored mixed complex of both the metals and dye; and (*3*) the formation of complicated mixed oxo complexes of zirconium and hafnium which have a higher stability than the zirconium complex of Methylthymol Blue. The last interpretation appears more plausible than the first two, but confirmation is needed.

CONCLUSION

Both Xylenol Orange and Methylthymol Blue are selective and sensitive reagents for zirconium and hafnium. The only interfering metals are the highly charged metal ions, some of which are easily masked by suitable complexing agents (Table I). In practical work, both zirconium and hafnium are conveniently co-precipitated with aluminum, titanium, and other metals which do not react with either Xylenol Orange or Methylthymol Blue in a strongly acidic medium. Such separation and determination with Xylenol Orange has been successfully applied to the determination of either traces of zirconium or hafnium in high temperature alloys[3,8]. Furthermore, for the first time zirconium and hafnium, present together in trace amounts, can be determined without physical separation. It is possible that the present approach may be applicable to other chromogenic reagents for zirconium and hafnium. Dyes related to Xylenol Orange and Methylthymol Blue such as Calcein (Fluorexon)[9], which forms greenish yellow complexes with zirconium and hafnium in a strong acidic medium, may deserve study. The nature of the bleaching reaction of hafnium on zirconium–dye complexes offers an interesting problem for future study.

ACKNOWLEDGEMENTS

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SUMMARY

Both Xylenol Orange and Methylthymol Blue are highly selective and sensitive reagents for zirconium and hafnium forming intensely red complexes in an acidic medium. The factors affecting the color formation have been studied. The properties of the complexes have been determined and compared. In general, zirconium forms a more stable complex with the two dyes than hafnium, and Xylenol Orange forms a stronger complex with either zirconium or hafnium than Methylthymol Blue. Hydrogen peroxide can completely mask the zirconium complexes of either dye but only slightly affects the hafnium complex of Xylenol Orange. Zirconium and hafnium can both be determined without separation using peroxide as a masking agent and sulfate as a demasking agent. A bleaching reaction was observed when small amounts of hafnium were added to the red zirconium complex of Methylthymol Blue in 2.4 *N* perchloric acid or a small amount of zirconium was added to the red hafnium complex of Methylthymol Blue solution at pH 2 to 3.

RÉSUMÉ

L'orangé de xylénol et le bleu de méthylène sont des réactifs très sélectifs et sensibles pour le zirconium et pour l'hafnium, formant des complexes d'un rouge intense, en milieu acide. D'autre part, le peroxyde d'hydrogène peut masquer complètement les complexes formés par le zirconium et chacun de ces deux réactifs, alors que le complexe hafnium–orangé de xylénol n'est que légèrement affecté. Il est alors possible de doser le zirconium et l'hafnium, l'un en présence de l'autre, sans séparation, en utilisant le peroxyde d'hydrogène, comme agent de masquage et l'acide sulfurique comme agent de "démasquage".

ZUSAMMENFASSUNG

Xylenolorange und Methylthymolblau sind hochselektive und empfindliche Reagenzien für Zirkonium und Hafnium, mit denen sie intensiv rot gefärbte Komplexe bilden. Die Faktoren, die die Farbbildung beeinflussen, wurden untersucht und die Eigenschaften der Komplexe bestimmt. Im Allgemeinen sind die Zirkonium-Komplexe mit den beiden Farbstoffen stabiler als die des Hafniums, und die Xylenolorange-Komplexe des Zirkoniums und Hafniums sind stabiler als die mit Methylthymolblau. Wasserstoffperoxyd kann die Zirkonium-Komplexe der beiden Farbstoffe vollständig maskieren, beeinflusst aber den Hafnium-Komplex mit Xylenolorange nur wenig. Zirkonium und Hafnium können nebeneinander bestimmt werden mit Wasserstoffperoxyd als Maskierungs- und Sulfat als Demaskierungsmittel. Eine bleichende Wirkung wurde beobachtet, wenn geringe Mengen Hafnium zu dem roten Zirkonium-Komplex mit Methylthymolblau in 2.4 *N* Perchlorsäure, oder eine geringe Menge Zirkonium zu dem roten Hafnium-Komplex mit Methylthymolblau bei pH 2–3 zugegeben wurde.

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DETERMINATION OF CADMIUM IN URANIUM BY ION EXCHANGE AND SQUARE-WAVE POLAROGRAPHY

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Cadmium has a high absorptive cross section for thermal neutrons, hence its concentration in uranium fuel must be carefully controlled. In many cases, cadmium which is contained as an impurity in reactor-grade uranium is specified to be below 0.1 or 0.2 p.p.m. Several instrumental methods have been applied for the determination of cadmium in uranium and its compounds. SCRIBNER AND MULLIN[1] developed an ingenious spectroscopic method for the determination of impurities including cadmium. FURMAN AND JENSEN[2] and MORIMOTO AND ASHIZAWA[3] determined cadmium colorimetrically with dithizone, and SAMBUCETTI *et al.*[4] and SAITO AND TAKEUCHI[5] applied polarography preceded by concentration at the mercury cathode or by solvent extraction. None of these methods, however, can be applied with sufficient sensitivity when quantities of cadmium below 0.1 p.p.m. are encountered. As regards more sensitive methods, the papers of NIKELLY AND COOKE[6] and of KEMULA *et al.*[7] may be mentioned; these workers proposed anodic-stripping polarography with the hanging mercury drop electrode, which required highly skilled techniques.

Square-wave polarography preceded by an anion-exchange separation provides a powerful tool for the determination of trace impurities in uranium. The present paper describes a method by which cadmium in uranium can be determined in the parts per hundred million range with accuracy and good reproducibility.

EXPERIMENTAL

Apparatus

Polarograph. The instrument used was a Mervyn-Harwell square-wave polarograph, Mark III, which was fitted with a water bath thermostatically controlled at 25 $\pm$ 0.2° and incorporating cells. At the maximum sensitivity it gives the peak height of about 75 divisions of the recorder scale for $8 \cdot 10^{-7}$ *M* cadmium in 1 *M* hydrochloric acid solution. The drop time of the dropping mercury electrode was maintained at 5 sec and the mercury pool anode was applied for each determination. Oxygen was removed from the solution with a stream of nitrogen purified by a reduced copper column[8].

Ion-exchange column. A bank of ion-exchange columns was constructed from glass tubes, 10 mm in internal diameter and 100 mm long, each having a 60-ml reservoir at the top and a stopcock at the lower end. The resin bed was supported on a loose plug of glass wool.

Reagents

Resin bed. Dowex 1 × 4, 50–100 mesh, analytical grade, chloride form, was thor-

oughly washed with water and 6 ml were transferred to the ion-exchange column. For the removal of impurities in the resin, the resin column was washed with 30 ml each of concentrated, 6 *M*, 3 *M*, and 1 *M* hydrochloric acid and 0.5 *M* nitric acid, successively. After being washed with water, the column was treated with 40 ml of 3 *M* hydrochloric acid to convert the resin to the chloride form and to be ready for use. After use, the resin column was washed with 0.5 *M* nitric acid and water and regenerated by passing through 40 ml of 3 *M* hydrochloric acid.

Cadmium-free uranium solution. A solution containing 2 g of uranium in 10 ml of 3 *M* hydrochloric acid was prepared by dissolving the appropriate amount of uranyl chloride (UO_2Cl_2, Yokosawa Chemicals Co., Tokyo, Japan). To remove cadmium, the solution was poured into the ion-exchange column and uranium was eluted with 1 *M* hydrochloric acid. The eluate was collected in a 100-ml beaker and evaporated nearly to dryness. The residue was dissolved in 10 ml of 3 *M* hydrochloric acid, and a cadmium-free uranium solution was obtained.

Cadmium solutions. A $1.00 \cdot 10^{-2}$ *M* stock solution was prepared by dissolving pure cadmium metal in hydrochloric acid. Standard working solutions of $1.00 \cdot 10^{-4}$ *M* and $1.00 \cdot 10^{-6}$ *M* were obtained by suitable dilution.

All the other reagents were prepared from reagent-grade chemicals. Distilled water purified by passing through a mixed-bed ion-exchange column was sufficiently pure for general use.

Recommended procedure

Weigh 2 g of the sample into a 100-ml conical flask and add 10 ml of distilled 6 *M* hydrochloric acid. Add drop by drop 10 ml of 30% hydrogen peroxide while heating the solution to boiling. Hold at this temperature until dissolution is complete, the excess hydrogen peroxide decomposes, and the solution is reduced to about 5 ml by evaporation. Cool to room temperature and dilute the solution with 5 ml of water.

Pour the resulting solution onto the ion-exchange column. Maintain the flow rate at 1 to 1.5 ml per min for this and succeeding steps. Elute the column with 40 ml of 1 *M* hydrochloric acid to remove most of the uranium and with 15 ml of 0.5 *M* nitric acid to remove the retarded uranium. With another 30 ml of 0.5 *M* nitric acid, elute the cadmium adsorbed in the resin and collect the eluate in a 100-ml beaker. Evaporate the eluate to dryness and add 2 ml of 1 *M* potassium chloride to dissolve the residue.

Transfer this solution to the polarograph cell already charged with mercury, deaerate for 10 min with nitrogen, and record the polarogram at an applied d.c. potential between −0.45 and −0.80 V *vs.* the mercury pool anode. Measure the peak height of the cadmium wave in divisions of the recorder scale and obtain the concentration with reference to calibration curves.

In order to determine the blank, carry the 10 ml of 6 *M* hydrochloric acid through the entire procedure. The blank is subtracted, and the cadmium content of the sample is obtained.

Preparation of the calibration curves

Using the standard working solution, transfer quantities of cadmium varying between 0.05 and 0.25 μg to a series of 100-ml beakers. Evaporate each solution to dryness and add 2 ml of 1 *M* potassium chloride to dissolve the residue. Record the polarogram and plot the peak height against the cadmium concentration.

RESULTS AND DISCUSSION

Separation of cadmium from uranium

A procedure for the separation of cadmium from uranium by means of cation-exchange resin has been described by STRELOW[9]. In order to separate traces of cadmium in uranium quantitatively, anion-exchange resin seemed to be more promising from the work of KRAUS AND NELSON[10] on the anion-exchange behavior of uranium (VI) and cadmium(II) in hydrochloric acid solutions.

The differences in adsorbability between uranium(VI) and cadmium(II) at low hydrochloric acid concentrations are sufficiently large to permit separation with a small column. If elution is carried out with 1 *M* hydrochloric acid, uranium(VI) can be removed while cadmium(II) is adsorbed strongly. Removal of cadmium(II) from the resin can be effected with water or other mineral acids such as nitric or perchloric acid.

Typical separations of cadmium and uranium are illustrated in Fig. 1. A 3 *M* hydrochloric acid solution containing 2 g of uranium and 1 μg of cadmium was prepared and transferred to the ion-exchange column. Uranium(VI), which forms a yellow band in the resin bed, was eluted with 40 ml of 1 *M* hydrochloric acid at a flow

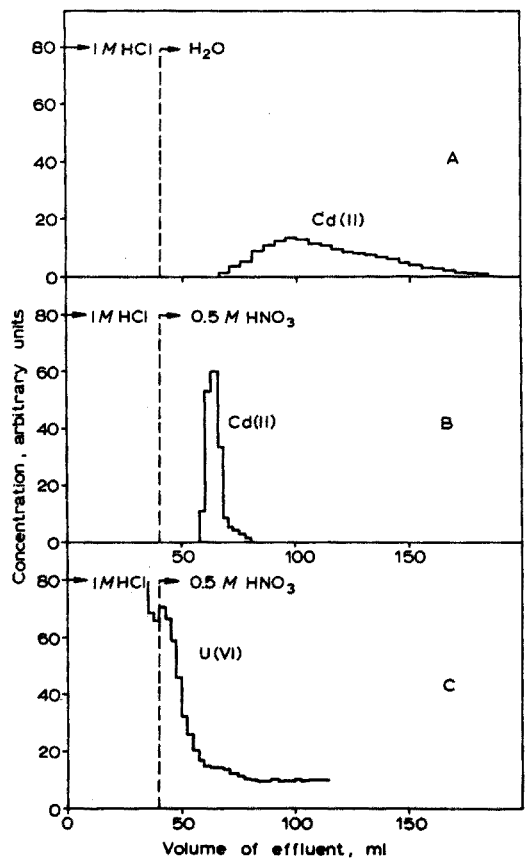

Fig. 1. Separations of cadmium(II) and uranium(VI).

rate of 1 ml per min. The cadmium adsorbed in the resin was eluted with water or with 0.5 *M* nitric acid at the same flow rate. The cadmium concentration in the effluent fractions was measured by the square-wave polarograph. Complete elution of cadmium(II) with water alone (see Fig. 1 A) requires inconveniently large volumes. On elution with 0.5 *M* nitric acid (see Fig. 1 B), cadmium(II) appears in a sharp band. The elution with the nitric acid is, therefore, more time-saving than that with water.

Small amounts of uranium still appeared in the eluate of 0.5 *M* nitric acid, even after the elution with the 1 *M* hydrochloric acid. An example of elution of uranium(VI) is illustrated in Fig. 1 C. Increasing the volume of 1 *M* hydrochloric acid to 80 ml did not improve the separation. Provided that the first 15-ml fraction of the effluent of 0.5 *M* nitric acid was separated from the following fractions, the uranium(VI) which appeared in the cadmium eluate could be minimized. Lead(II), which is contained in the sample and the reagents used, also appeared in the cadmium eluate. Complete elimination of lead(II) and uranium(VI) from the cadmium eluate could not be achieved by the present procedure. However, cadmium can be selectively determined by the square-wave polarograph as is shown in the following discussion.

Supporting electrolyte

Because of the incomplete separations, it is necessary to determine cadmium in the presence of uranium and lead which are in slightly higher concentration than cadmium. With the square-wave polarograph, all of these three elements produce well-defined peaks from a variety of supporting electrolytes.

The supporting electrolytes examined here were 1 *M* hydrochloric acid, 0.1 *M* hydrochloric acid – 1 *M* potassium chloride, and 1 *M* potassium chloride. The measurements were carried out at concentrations of $1 \cdot 10^{-6}$ *M* cadmium, $2 \cdot 10^{-5}$ *M* lead

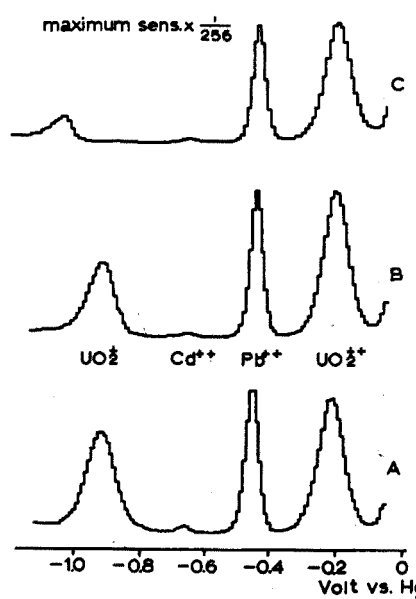

Fig. 2. Square-wave polarograms for $1 \cdot 10^{-6}$ *M* Cd^{2+}, $2 \cdot 10^{-5}$ *M* Pb^{2+}, and $1 \cdot 10^{-4}$ *M* UO_2^{2+} in 1 *M* HCl (A), 0.1 *M* HCl + 1 *M* KCl (B), and 1 *M* KCl (C).

and $1 \cdot 10^{-4}$ *M* uranium, these being of approximately the same order as the concentrations of the eluate obtained by the separation procedure. Typical polarograms are shown in Fig. 2. Uranyl ion gives two peaks; the first peak corresponds to the reduction of uranium(VI) to uranium(V), and the second peak to the reduction of uranium(V) to uranium(III). The second peak in 1 *M* potassium chloride is lower and shifts to a more negative potential than that in the acidic chloride solutions. The lead peak appears at −0.44 V *vs.* the mercury pool anode. Cadmium gives a peak between the lead and the second uranium peaks, at a potential of −0.62 V *vs.* the mercury pool anode. The cadmium peaks recorded at the higher instrument sensitivity are shown in Fig. 3. In both 1 *M* hydrochloric acid and 0.1 *M* hydrochloric acid – 1 *M* potassium

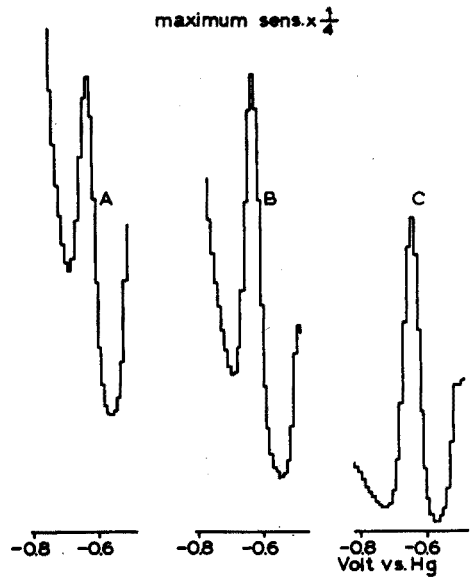

Fig. 3. Square-wave polarograms for $1 \cdot 10^{-6}$ *M* Cd^{2+} in the presence of $1 \cdot 10^{-4}$ *M* UO_2^{2+} and $2 \cdot 10^{-5}$ *M* Pb^{2+} in 1 *M* HCl (A), 0.1 *M* HCl + 1 *M* KCl (B), and 1 *M* KCl (C).

chloride, the peak potentials of cadmium and uranium (the second peak) are too close together for proper determinations. In 1 *M* potassium chloride, however, the cadmium peak is clearly separated from both the lead and the second uranium peaks and can be easily measured without interference. The 1 *M* potassium chloride is, therefore, well suited to the determination of cadmium in the present method. With this supporting electrolyte, calibration curves were prepared at several instrument sensitivities. A linear relation is obtained between the concentration and the peak height.

Accuracy and precision

To evaluate the method, synthetic samples were prepared by adding known amounts of cadmium to a cadmium-free uranium solution and were analyzed as described in the recommended procedure. The results are shown in Table I, in which the blank value, 0.008 p.p.m., has been subtracted. The agreement between the added and the found

values indicates that cadmium is separated by the ion-exchange procedure with 100% efficiency and that the present technique offers an accurate method for determining cadmium in uranium.

Seven replicate determinations were conducted on a uranium dioxide sample. The data are shown in Table II.

TABLE I

DETERMINATION OF CADMIUM IN SYNTHETIC SAMPLES

Cd added (p.p.m.)	*Cd found (p.p.m.)*	*Mean of Cd found (p.p.m.)*	*Deviation (p.p.m.)*
0.028	0.027 0.028 0.028	0.028	0.000
0.056	0.055 0.063 0.053	0.057	+0.001
0.112	0.112 0.107 0.128	0.116	+0.004

TABLE II

REPRODUCIBILITY OF RECOMMENDED PROCEDURE

Sample no.	*Cd found (p.p.m.)*
1	0.065
2	0.073
3	0.080
4	0.075
5	0.073
6	0.060
7	0.091
Mean	0.074
Standard deviation	± 0.009 (±12%)

TABLE III

DETERMINATION OF CADMIUM IN URANIUM DIOXIDE SAMPLES

Sample		*Sample taken (g)*	*Cd found* (p.p.m.)*
Reactor-grade	A	2	<0.01
	B	2	<0.01
	C	2	0.076
	D	1	0.082
Reagent-grade	E	0.1	1.45

* Mean value of three determinations.

Analytical results

The method was applied to several reactor-grade and reagent-grade uranium dioxide samples, with the results given in Table III. The cadmium content of all reactor-

grade samples analyzed here was less than 0.1 p.p.m. The described procedure offers a sensitive method for determining trace cadmium in uranium dioxide. The method may also be applicable to metallic uranium, its compounds, and some of its alloys. Once the calibration curve has been established and a bank of the ion-exchange columns has been prepared, many determinations can be performed simultaneously within 4 h. This method is rather time-consuming, but more sensitive than the others available. Other impurities in uranium do not interfere in this method.

ACKNOWLEDGEMENTS

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SUMMARY

Traces of cadmium in uranium and its compounds can be determined by ion-exchange separation and square-wave polarography. With a small column of anion-exchange resin, cadmium can be separated from uranium and recovered quantitatively from hydrochloric acid solution. Separations of cadmium from uranium are not perfect but are sufficient for the determination of traces of cadmium by square-wave polarography. The lower limit of the method is 0.01 p.p.m. of cadmium.

RÉSUMÉ

Une méthode est décrite pour le dosage de traces de cadmium dans l'uranium et ses composés. La séparation se fait sur résine échangeur d'ions et le dosage par polarographie à ondes carrées. Il est possible de déterminer ainsi des teneurs en cadmium de 0.01 μg/g.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Spuren von Cadmium in Uran und seinen Verbindungen beschrieben. Sie beruht auf der Trennung mit Hilfe eines Ionenaustauscherharzes und anschliessend polarographischer Bestimmung. Nach dieser Methode können noch 0.01 μg/g Cadmium bestimmt werden.

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COLOUR REACTION OF SCANDIUM WITH QUERCETIN AND ITS APPLICATION TO THE ANALYSIS OF SCANDIUM

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Quercetin (3, 3', 4', 5, 7-pentahydroxyflavone) reacts with several metal ions to give coloured compounds which have been used for the colorimetric determination of micro-amounts of metals. OKA AND MATSUO[1] have described the determination of germanium with quercetin as colorimetric reagent. GRIMALDI[2] studied the reaction of quercetin with zirconium and showed that 1:1 and 2:1 complexes were formed. According to KOMENDA[3], uranium reacts with quercetin at pH 7 to give a brown complex, while cerium forms a violet complex in neutral and acid solutions. MENIS, MANNING AND GOLDSTEIN[4] have determined thorium with quercetin and have described a separation scheme for interfering ions. The reaction between quercetin sulphonate and thorium has also been applied colorimetrically by KANNO[5], who found that the complex contained quercetin and thorium in the ratio of 1:1 at pH 6.3 and 1:2 at pH 5.0, and that the molar extinction coefficient of the complex was 33,000.

Scandium has very few characteristic and sensitive colour reactions. Alizarin red S appears to be the only colour reagent that has been utilized successfully[6]. Scandium also gives a sensitive fluorescence reaction with morin in neutral or weakly acidic solution[7]. In the present study quercetin, an isomer of morin, was examined as a possible colorimetric reagent for scandium. Like the other reagents for scandium, quercetin is sensitive but not at all selective.

EXPERIMENTAL

Apparatus and reagents

A Hitachi EPU-2A spectrophotometer with 1-cm quartz cells was used for all absorbance measurements. For pH measurements a glass electrode pH meter (Toa Dempa Model HM-5) was used.

Quercetin solution. Dissolve a suitable amount of quercetin (G.R. grade, Tokyo Kasei Co. Ltd.) in 95 % ethyl alcohol. The concentration used in the recommended procedure was 0.1 %.

Scandium stock solution. Dissolve 319.6 mg of air-dried Sc_2O_3 (G.R. grade, Yokozawa Chemical Co.) in perchloric acid, by warming on a water bath. After cooling, dilute the solution to 100 ml with water. This solution contained 526.7 μg of scandium per ml. Less concentrated solutions were made by appropriate dilution of the stock solution.

Buffer solutions were prepared by mixing 0.1 *N* ammonium acetate and 0.1 *N* acetic acid solutions for acidic pH, or 0.1 *N* ammonium chloride and 0.1 *N* ammonia solutions for alkaline pH. The strong basic anion-exchange resin, Diaion SA 100, (analytical grade, 100 to 200 mesh) was used in the separation. All other reagents used were of G. R. grade purity.

Procedure

Prepare a solution that contains 18 to 75 μg of scandium in a volume of about 5 ml and add 10 ml of 95 % alcohol. Adjust the pH to 4.4 by acetate buffer solution. Add 2 ml of 0.1 % quercetin solution. Dilute to 25 ml with water. Mix the solution and the colour will develop in a few minutes, then measure the absorbance against a reagent blank at 435 mμ. Heating of solution before absorbance measurements is not needed. It is recommended that the coloured solution be allowed to stand for several minutes until bubbles in solution have disappeared.

RESULTS AND DISCUSSION

Absorption spectra

To determine the optimum pH value for colour development, a series of solutions

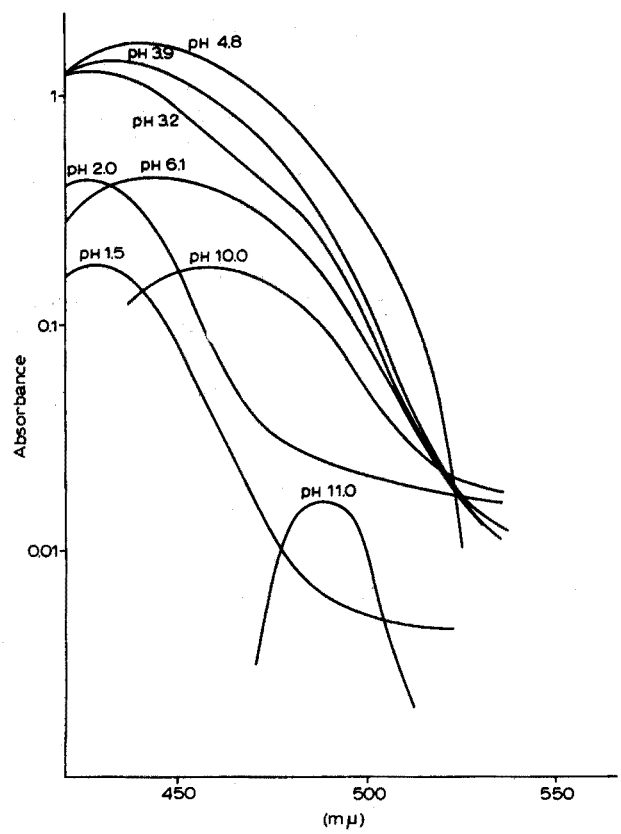

Fig. 1. Absorption spectra for scandium–quercetin complex at various pH. Concentration of scandium: $2.4 \cdot 10^{-6}$ *M*.

that contained the same amounts of scandium and quercetin, and differed only in pH value was prepared. The absorption spectrum of each solution was measured against the reagent blank. The results are shown in Fig. 1. The spectra exhibit absorption between 400 and 500 mμ with a maximum between 430 and 450 mμ. A wavelength of 435 mμ was chosen for practical measurements. The absorption spectra of the complex indicate essentially the same shape over the pH range of 3.2 to 4.8. At higher and lower pH values, the absorbances diminish and the absorption spectra change their shape. Consequently only one species of complex is probably present, at least in the pH range between 3.2 and 4.8.

Effect of reagent concentration

In order to study the effect of reagent concentration on the absorbance, 52.7 μg of scandium was added to solutions containing various amounts of quercetin and the same amounts of buffer solution. Absorbances were measured after dilution to 25 ml. The reagent concentration did not influence the absorbance when more than 1 ml of 0.1 % quercetin solution was present. The use of 2 ml of the reagent is recommended.

Effect of ethyl alcohol

As quercetin and the scandium–quercetin complex are only partially soluble in water, ethyl alcohol is required to increase the solubility of the complex. The same conditions as in the preceding section, except for the volumes of ethyl alcohol, were adopted. If less than 3 ml of alcohol was used, the solutions became turbid. The absorbances were constant when 10 to 12 ml of ethyl alcohol were added, but decreased on addition of amounts of ethyl alcohol outside this range.

Conformity to Beer's law

The linearity between the absorbance of scandium–quercetin complex and the scandium concentration was tested by varying the scandium concentration and measuring the absorbances at 435 mμ and pH 4.4. Conformity to Beer's law was found over a range of 0.1 to 3 p.p.m. of scandium. The molar extinction coefficient at 435 mμ is 12,800.

The optimum range of scandium to realize maximum precision was determined by a Ringbom and Ayres plot; 18 to 75 μg of scandium can be analysed with maximum precision. The relative analysis error for a 1 % absolute photometric error was calculated as 2.8 %.

The composition of quercetin complex of scandium

To estimate the empirical formula of the complex species formed under the present conditions, the continuous variation[8] and slope ratio[9] methods were used. For the former method, solutions of scandium and quercetin of the same concentration were mixed in varying proportions, and the series of solutions thus prepared was adjusted to pH 4.4 and measured at 435 mμ. Fig. 2 shows that the combining ratio of quercetin to scandium can be reasonably regarded as 1 to 1. In the slope ratio method, two series of solutions were prepared; in the first, various amounts of scandium were added to a large excess of quercetin, and in the second, different quantities of quercetin were added to a large excess of scandium. The absorbances of the solutions

were measured and plotted against the concentration of the variable component. The combining ratio in the complex is equal to the ratio of the slopes of the two straight lines which are shown in Fig. 3. The calculated ratio is also 1 which indicates the formation of the 1:1 species.

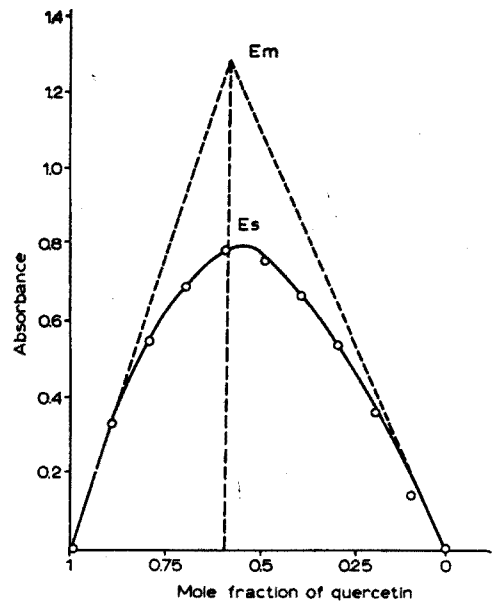

Fig. 2. Continuous variation plot for scandium–quercetin complex.

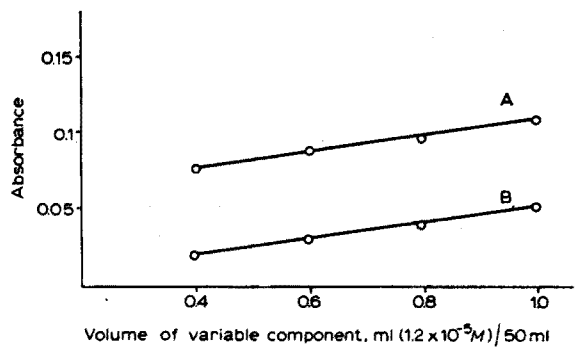

Fig. 3. Slope ratio plot for scandium–quercetin complex. A: quercetin constant, $2.4 \cdot 10^{-6}$ *M*, B: scandium constant, $2.4 \cdot 10^{-6}$ *M*.

The "gerade" method proposed by ASMUS[10] also suggests the existence of a 1:1 species in the solution.

Spectrophotometric determination of instability constant

As the combining ratio of scandium–quercetin complex is 1:1, the dissociation of the complex can be expressed as:

$$Sc\text{-}Q \rightleftarrows Sc + Q$$

If c is taken as the total concentration of complex and α as the degree of dissociation, the instability constant is expressed as follows,

$$K = \frac{(\alpha c)^2}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha}$$

The apparent overall instability constant of the complex can easily be calculated from the measurement of the degree of dissociation. The value of α is obtained from the relationship:

$$\alpha = \frac{E_m - E_s}{E_m}$$

where E_m is the maximum absorbance of the complex when it does not dissociate into metal ions and free ligands, and E_s is the actual absorbance of the complex. E_m and E_s are introduced from the continuous variation plots. E_s is the actual maximum point on the continuous variation plot. E_m can be obtained graphically from the same plot as the intercept of the two slopes which are tangents of the continuous variation curve at the points that the mole fraction of quercetin is zero and one (Fig. 2). The apparent instability constant of scandium–quercetin complex at room temperature is thus estimated to be $2.7 \cdot 10^{-7}$.

Effect of diverse ions

Nickel(II), iron(III), chromium(VI), chromium(III), uranium(VI) and aluminum(III) as well as thorium(IV) seriously interfere, as is pointed out by MENIS *et al.*[4]. The interference from iron(III) can be avoided completely by reduction to iron(II) with ascorbic acid or hydroxylamine. Of the common anions, nitrate, thiocyanate, perchlorate, acetate and chloride do not interfere. Phosphate, sulphate, citrate, tartrate and oxalate must be absent. A detailed account of the separation of scandium from interfering ions will be published later, but the applicability of anion-exchange separation techniques was tested preliminarily.

Separation of scandium

The sample solution is placed on a hot plate, and evaporated to dryness. After cooling, the residue is dissolved in 13 *N* hydrochloric acid solution. This solution is added to a column (1 × 15 cm) of strong basic anion exchanger (Diaion SA 100, 100–200 mesh, Cl-form) pretreated with 13 *N* hydrochloric acid. Then, the elution is carried out with 20 ml of 13 *N* hydrochloric acid. Scandium and thorium are eluted with 10 ml of 6 *N* hydrochloric acid. This solution is evaporated to dryness and the

TABLE I

RECOVERY OF SCANDIUM AFTER ION-EXCHANGE SEPARATION

Diverse ions	*Amount of ion (mg)*	*Scandium (μg)*	
		present	*recovered*
Fe(III)	10	105	98
Th(IV)	1	105	97
Th(IV)	0.5	105	96
Al(III)	1	105	90
La(III)	1	105	85

residue is cooled and dissolved in 8 *N* nitric acid. This solution is placed on another column (1 × 17 cm) containing the same anion exchanger as above (NO_3-form) pretreated with 8 *N* nitric acid. The elution is carried out with 10 ml of 8 *N* nitric acid. The solution obtained is evaporated to dryness. The residue is dissolved in small amounts of hot water containing a few drops of 0.1 *N* perchloric acid, and the procedure for the determination is applied as for solutions of pure scandium.

When 13 *N* hydrochloric acid is used as eluant, lanthanons and aluminum are eluted, whereas scandium, thorium and iron are retained on the resin[11]. Scandium and thorium are then eluted with 6 *N* hydrochloric acid, and iron remains on the column. Separation of scandium from thorium is effected by the difference in absorbability of their nitrate complexes on anion exchangers.

The results for the separation of 105 μg of scandium from milligram amounts of aluminum, iron, lanthanum and thorium before the colorimetric determination with quercetin are given in Table I. Some loss of scandium is apparent, particularly in the separation from lanthanum and aluminum.

Another new method using a cation exchanger was developed for the separation of scandium from lanthanum and thorium. The solution containing scandium and lanthanum is placed on a column (1 × 5 cm) of strong acidic cation exchanger (Diaion SK1, 100–200 mesh, H-form). Scandium is eluted with 15 ml of 2 % oxalic acid solution; lanthanum remains on the column. A few mg of scandium can be completely separated from 100 mg of lanthanum. The method could be extended to separate scandium from rare earth elements other than lanthanum. Separation of scandium from thorium is possible when a mixture of ammonium oxalate and acetate (3 % ammonium oxalate and 1 % ammonium acetate) is used as eluant. A mixture of 4.05 mg of scandium and 11.25 mg of thorium is placed on the top of the column

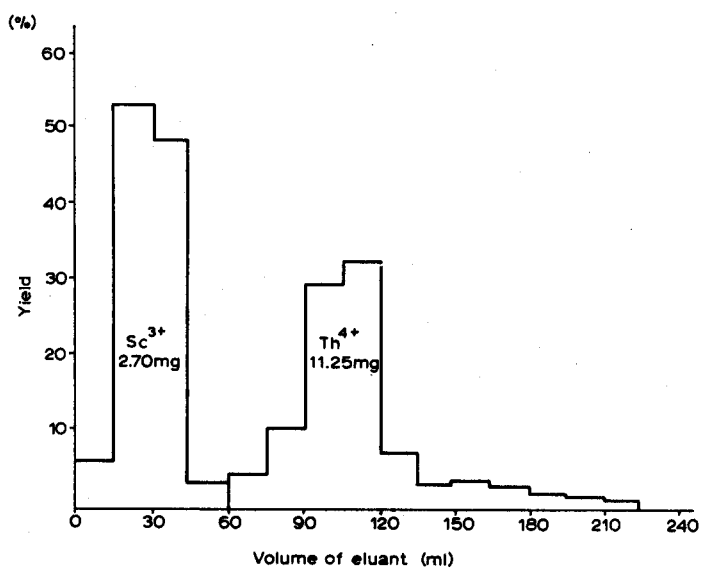

Fig. 4. Elution curve of scandium and thorium.

(1 × 24 cm) of the resin (Diaion SK1, 100–200 mesh, H-form). The elution of thorium begins after scandium has been completely eluted. The elution curves of scandium and thorium are shown in Fig. 4. The behaviour of scandium oxalate with the cation exchanger is of particular interest in developing the separation scheme for scandium.

SUMMARY

A spectrophotometric study of the scandium–quercetin complex is described; μg amounts of scandium can be determined with quercetin at 435 mμ and pH 4.4. A 1:1 complex is formed. The apparent instability constant of the complex was estimated as $2.7 \cdot 10^{-7}$ by a spectrophotometric method. An ion-exchange method for separating scandium from several interfering ions is described.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Komplex Scandium–Quercetin und dessen Anwendung zur spektrophotometrischen Bestimmung von Scandium. Störende Ionen werden mit einem Austauscherharz entfernt.

RÉSUMÉ

Les auteurs ont effectué une étude du complexe scandium–quercétine. Une méthode de dosage est décrite, ainsi qu'une méthode de séparation d'avec de nombreux ions gênants, par échangeur d'ions.

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THE WET CHEMICAL ANALYSIS OF CERTAIN IMPURITIES IN HIGH-PURITY BERYLLIUM*

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Recent developments in purifying beryllium by vacuum distillation[1] and by zone refining[2] have resulted in beryllium in which the level of most impurity elements is 10 p.p.m. or less. A review of existing wet chemical methods indicated that, in the range of 1 to 10 p.p.m., most analyses were not sufficiently sensitive. The sensitivity necessary for analysis in this range could not be obtained by the simple expedient of using a larger beryllium sample.

Therefore, a research program to find wet chemical methods suitable for the analysis of trace impurities in beryllium was undertaken. The methods developed in this program are described in detail below. Spectrophotometric procedures are applied. Iron is determined by extraction of iron-bathophenanthroline, nickel by extraction of nickel-furildioxime, copper by extraction of copper-neocuproine, and aluminum by extraction of aluminum-hydroxyquinoline. Silicon is determined by the formation of silico-molybdenum blue and chromium with diphenylcarbazide. Manganese is determined by extraction of its chelate with 1-(2-pyridylazo)-2-naphthol (PAN).

THE DETERMINATION OF IRON[3]

Reagents

Bathophenanthroline solution (obtained from G. Frederick Smith Chemical Company). Dissolve 0.0664 g of the solid in 200 ml of 95% ethyl alcohol.

Sodium acetate solution (3 M). After dissolution of 246 g of the salt in 1 l of water, to each 200 ml add 10 ml of 10% (w/v) hydroxylamine hydrochloride and 10 ml of bathophenanthroline. Extract twice with 15-ml portions of nitrobenzene to purify the sodium acetate.

Procedure

The sample may be dissolved in dilute hydrochloric or sulfuric acid. The amount of free acid must be minimized. The total amount of concentrated acid is 7 ml of sulfuric acid or 21 ml of hydrochloric acid per gram of beryllium.

After dissolution of the sample, a stock solution is made up so that aliquots can be taken to contain up to 0.5 g of sample in a volume no greater than 25 ml. To this aliquot in a beaker add 2 ml of 10% (w/v) hydroxylamine hydrochloride solution,

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5 ml of bathophenanthroline solution, and 20 ml of sodium acetate solution. The pH should now be between 4.0 and 5.5. Adjust to pH 4.0 by adding hydrochloric acid. Transfer the solution to a 125-ml separatory funnel. Add 10 ml of nitrobenzene and shake for 1 min. Allow the layers to separate and reserve the lower layer in a dry 25-ml volumetric flask. Repeat the extraction with a second 10 ml portion of nitrobenzene. Dilute to volume with absolute ethyl alcohol.

Prepare a blank by adding the equivalent amount of water used in the sample aliquot and adding the acid and other reagents as described above. Follow the same extraction procedure as for the samples.

Determine the optical densities of the blank and samples on a Beckman DU Spectrophotometer with 5-cm cells at a wavelength of 538 mμ with water in the reference cell. After the average optical density of the blank has been deducted from that of the samples, the corrected optical densities are compared to a standard curve obtained for 0.5–10 μg of iron. Results for iron with and without added beryllium are shown in Table I.

TABLE I

IRON BY THE BATHOPHENANTHROLINE METHOD

Fe (μg)	*Distilled Be (mg)*	*O.D.*	*O.D. minus average blank*	*O.D. per μg Fe*
0.0	0	0.183		
	0	0.178		
2.5	0	0.390	0.210	0.0840
	0	0.385	0.205	0.0820
5.0	0	0.590	0.410	0.0820
	0	0.598	0.418	0.0836
10.0	0	1.005	0.825	0.0825
	0	1.003	0.823	0.0823
0.0	380	0.306		
	380	0.305		
2.5	380	0.513[a]	0.207	0.0828
	380	0.515[a]	0.209	0.0836
0.0	220	0.253		
	220	0.252		
5.0	220	0.670	0.418[a]	0.0836
	220	0.668	0.416[a]	0.0832

[a] Minus average O.D. for unspiked beryllium samples.

THE DETERMINATION OF NICKEL[4]

Reagent

α-Furildioxime solution. Dissolve 1 g of α-furildioxime in 100 ml of 50% ethyl alcohol.

Procedure

After dissolution of the sample as described for the determination of iron, a stock solution is made up so that aliquots can be taken to contain up to 0.25 g of sample in a volume no greater than 25 ml. To this aliquot in a 125-ml separatory funnel add 10 ml of 30% (w/v) sodium citrate solution, 5 drops of 1% phenolphthalein in

95% ethyl alcohol, and 10 drops of concentrated ammonium hydroxide. Add 20% (w/v) sodium hydroxide solution until a permanent pink develops, then add 10 drops more of ammonium hydroxide. Add 3 ml of α-furildioxime solution and 10 ml of chloroform. Shake for 1 min and reserve the lower layer in a dry 25-ml volumetric flask. Repeat the extraction by shaking the aqueous layer with another 10 ml portion of chloroform for 30 sec. Dilute to volume with absolute ethyl alcohol.

Prepare a blank by taking a similar aliquot of the dissolution acid and follow the procedure described above for the color development and extraction of the sample.

Determine the optical densities of the blank and samples on a Beckman DU Spectrophotometer with 5-cm cells at a wavelength of 435 mμ with water in the reference cell. After the average optical density of the blank has been subtracted from that of the samples, the corrected optical densities are compared to a standard curve obtained with 1–15 μg of nickel. Optical densities for varying amounts of nickel in the presence and absence of beryllium are shown in Table II.

TABLE II

NICKEL BY THE α-FURILDIOXIME METHOD

Ni (μg)	*Distilled Be (mg)*	*O.D.*	*O.D. minus average blank*	*O.D. per μg Ni*
0.0	0	0.067		
	0	0.064		
5.0	0	0.347	0.281	0.0562
	0	0.341	0.275	0.0550
10.0	0	0.621	0.555	0.0555
	0	0.625	0.559	0.0559
15.0	0	0.905	0.839	0.0559
	0	0.900	0.834	0.0556
0.0	203	0.082		
	203	0.076		
10.0	203	0.635	0.556[a]	0.0556
	203	0.637	0.558[a]	0.0558

[a] Minus average O.D. for unspiked beryllium samples.

THE DETERMINATION OF COPPER[5]

Reagent

Neocuproine solution. Dissolve 0.500 g of neocuproine (obtained from G. Frederick Smith Chemical Company) in 500 ml of ethyl alcohol (95%).

Procedure

After dissolution of the sample as described for the determination of iron, a stock solution is made up so that aliquots can be taken containing up to 0.25 g of sample in a volume no greater than 25 ml. To this aliquot in a beaker add 10 ml of 25% (w/v) hydroxylamine hydrochloride solution, 20 ml of 30% (w/v) sodium citrate solution, and 10 ml of neocuproine solution. Adjust the pH to 5.0 to 5.5 with ammonium hydroxide or hydrochloric acid as needed. Transfer the solution to a 125-ml separatory funnel. Add 10 ml of chloroform and shake for 45 sec. Reserve the lower layer in a 25-ml volumetric flask (previously dried) containing 4 ml of absolute ethyl

alcohol. Repeat the extraction with 5 ml of chloroform. Dilute to volume with absolute ethyl alcohol.

Prepare a blank by taking a similar aliquot of the acid used in dissolution of the sample and follow the procedure described above for the color development and extraction of the sample.

Determine the optical densities of the blank and samples on a Beckman DU Spectrophotometer with 5-cm cells at a wavelength of 457 mμ with water in the reference cell. After the average optical density of the blank has been deducted from that of the samples, the corrected optical densities are compared to a standard curve obtained with 1–30 μg of copper. Optical densities for copper in the presence and absence of beryllium are shown in Table III.

TABLE III

COPPER BY THE NEOCUPROINE METHOD

Cu (μg)	*Distilled Be (mg)*	*O.D.*	*O.D. minus average blank*	*O.D. per μg Cu*
0.0	0	0.099		
	0	0.101		
5.0	0	0.220	0.120	0.0240
	0	0.220	0.120	0.0240
10.0	0	0.353	0.253	0.0253
	0	0.355	0.255	0.0255
15.0	0	0.476	0.376	0.0251
	0	0.475	0.375	0.0250
20.0	0	0.606	0.506	0.0253
	0	0.608	0.508	0.0253
0.0	256	0.162		
	256	0.162		
10.0	256	0.414	0.252[a]	0.0252
	256	0.417	0.255[a]	0.0253

[a] Minus average O.D. for unspiked beryllium samples.

THE DETERMINATION OF ALUMINUM[6]

Reagents

o-Phenanthroline solution (0.025%). Dissolve 0.125 g of *o*-phenanthroline in 500 ml of water by shaking for several hours.

Sodium acetate–hydroxide solution. Mix three parts of 3 *M* sodium acetate (anhydrous) and one part of 4 *M* sodium hydroxide solutions.

8-Hydroxyquinoline solution. Dissolve 5 g of 8-hydroxyquinoline in 25 ml of glacial acetic acid. Dilute to 500 ml with water.

Procedure

After dissolution of the sample as described for the determination of iron, a stock solution is made up such that aliquots can be taken to contain 0.10 g of sample in a volume no greater than 25 ml. To this aliquot in a beaker add 2 ml of 10% (w/v) hydroxylamine hydrochloride solution, 2 ml of *o*-phenanthroline solution, and 10 ml of sodium acetate–hydroxide solution. Adjust the pH to 5.0 with a few drops of hydrochloric acid and transfer to a 125-ml separatory funnel. Add 3 ml of 8-hydro-

xyquinoline solution and 10 ml of chloroform. Shake for 2 min. Allow the layers to separate and drain into a dry 25-ml volumetric flask containing 1.0 g of anhydrous sodium sulfate. Repeat the extraction using 3 ml of 8-hydroxyquinoline solution and 10 ml of chloroform. Dilute to volume with chloroform.

Prepare a blank by using an aliquot, 0.1 *N* in acid, of the water and acid employed in the dissolution of the sample and follow the procedure described for the color development and extraction of the sample.

Prepare a standard curve by following the procedure used for sample preparation on aliquots containing 0.10 g of Pechiney super-purity flake beryllium* (obtained from General Astrometals Corporation, Yonkers, New York) and 1–15 μg of aluminum. Present indications are that a standard aluminum curve in the presence of beryllium is slightly less sensitive than an aluminum curve without beryllium (Table IV). Therefore, the curve was prepared using 0.100 $\pm$ 0.005 g of beryllium and sample aliquots are taken to contain the same amount of beryllium.

TABLE IV

ALUMINUM BY THE 8-HYDROXYQUINOLATE METHOD

Al (μg)	*Distilled Be* (mg)	*O.D.*	*O.D. minus average blank*	*O.D. per* μg *Al*
0.0	0	0.150		
	0	0.148		
5.0	0	0.377	0.228	0.0456
	0	0.377	0.228	0.0456
10.0	0	0.596	0.447	0.0447
	0	0.617	0.468	0.0468
15.0	0	0.855	0.706	0.0470
	0	0.835	0.686	0.0457
0.0	102	0.153		
	102	0.155		
5.0	102	0.378	0.224[a]	0.0448
	102	0.378	0.224[a]	0.0448
10.0	102	0.589	0.435[a]	0.0435
	102	0.592	0.438[a]	0.0438
15.0	102	0.818	0.664[a]	0.0443
	102	0.830	0.676[a]	0.0451

[a] Minus average O.D. for unspiked beryllium samples.

Determine the optical densities of the blank and samples on a Beckman DU Spectrophotometer with 5-cm cells at a wavelength of 392 mμ with water in the reference cell. After the average optical density of the blank has been deducted from that of the samples, the corrected optical densities are compared to a standard curve prepared from 1–20 μg of aluminum and 0.10 g of beryllium.

THE DETERMINATION OF SILICON

Apparatus

Polyethylene beakers with lids and polyethylene bottles for storage of solutions.

* A typical aluminum analysis reported by the supplier is 10 p.p.m.

Reagents

Molybdic acid solution (10%). Dissolve 25 g of ammonium molybdate tetrahydrate in about 200 ml of water. Cool, add 20 ml of 1:1 sulfuric acid and dilute to 250 ml.

Reducing solution. Dissolve 27 g of sodium bisulfite, 2 g of sodium hydroxide, and 0.5 g of 1-amino-2-naphthol-4-sulfonic acid in water. Dilute to 500 ml in a polyethylene beaker.

Boric acid solution (saturated). Dissolve 52.5 g of boric acid in warm water and dilute to 1 l.

Hydrofluoric acid (10% by weight). Weigh 104 g of 48% hydrofluoric acid, and dilute to 500 ml in a polyethylene bottle.

Standard silicon solution (1 μg Si/ml). Fuse 0.0862 g of N.B.S. No. 81 glass sand with 10 g of sodium carbonate in a platinum crucible. Dissolve the cooled melt in 500 ml of hot water in a large porcelain casserole. After cooling, transfer the solution to a 1-l volumetric flask. While swirling the solution in the flask, add very slowly 180 ml of 1:1 nitric acid. Cool, dilute to the mark with water, and mix well. From this stock solution, prepare a solution containing 1 μg of silicon per ml, adjusted to pH 1.0 with nitric acid.

Procedure

Weigh a 1.0 g sample of beryllium and place in a 400-ml polyethylene beaker. Add 25 ml of water and then 15 ml of nitric acid in small increments. If necessary, add a few drops of sulfuric acid and heat the sample to obtain complete dissolution. Add 5 ml of the 10% hydrofluoric acid and digest on a sand bath for 1 h. (Do not heat over 70°.) Cool, add 50 ml of saturated boric acid solution, and adjust the pH to 1.0 with nitric acid. Transfer to a 250-ml volumetric flask, wash, and dilute to

TABLE V

SILICON BY THE MOLYBDENUM-BLUE METHOD

Si (μg)	*Distilled Be (mg)*	*O.D.*	*O.D. minus average blank*	*O.D. per μg Si*
0.0	0	0.024		
	0	0.028		
5.0	0	0.231	0.205	0.0410
	0	0.222	0.196	0.0392
10.0	0	0.428	0.402	0.0402
	0	0.434	0.408	0.0408
15.0	0	0.632	0.606	0.0404
	0	0.640	0.614	0.0409
20.0	0	0.832	0.806	0.0403
	0	0.838	0.812	0.0406
25.0	0	1.038	1.012	0.0405
	0	1.033	1.007	0.0403
0.0	107	0.082		
	107	0.081		
10.0	107	0.493	0.411[a]	0.0411
	107	0.497	0.418[a]	0.0415
	107	0.488	0.406[a]	0.0406
	107	0.488	0.406[a]	0.0400

[a] Minus average O.D. for unspiked beryllium samples.

volume with a nitric acid solution of pH 1.0. Transfer a suitable aliquot to a 100-ml volumetric flask*. Add 50 ml of a nitric acid solution of pH 1.5 and then add 4 ml of molybdic acid solution. Allow to stand for 10 min. Add 10 ml of 20% (w/v) tartaric acid solution, and immediately add 2 ml of reducing solution. Let stand for 2 h. Dilute to volume with a nitric acid solution of pH 1.5. Mix well and read the blank and samples in 5-cm cells at 820 mμ. After the optical density of the blank has been subtracted from that of the samples, the corrected optical densities are compared to a standard curve obtained with 0–25 μg of silicon.

For the preparation of the standard curve, transfer 0, 5, 10, 15, 20 and 25 ml aliquots (0, 5, 10, 15, 20 and 25 μg of silicon) of standard silicon solution to 100-ml volumetric flasks. Adjust the volume to 25 ml with nitric acid (pH 1.0) solution. Add 50 ml of nitric acid (pH 1.5) solution, then add 4 ml of 10% molybdic acid solution. After 10 min add 10 ml of 20% (w/v) tartaric acid solution and immediately afterwards add 2 ml of reducing solution. Let stand for 2 h. Dilute to volume with nitric acid (pH 1.5) solution and mix well. Measure the optical densities in the 5-cm cells at 820 mμ. From these measurements construct the standard optical density–concentration curve. Results are shown in Table V.

THE DETERMINATION OF CHROMIUM[7]

Reagents

s-Diphenylcarbazide solution (0.4 %). Dissolve 0.2 g of *s*-diphenylcarbazide in 50 ml of acetone. Prepare fresh daily.

Potassium permanganate solution (0.25 N). Dissolve 0.675 g of the salt in 100 ml of water.

Procedure

The sample is dissolved as described for the determination of iron. If hydrochloric acid is used, the solution must be taken to fumes of sulfur trioxide to remove chloride ions.

After dissolution of sample, a stock solution is made up such that aliquots can be taken to contain up to 0.5 g of sample in a volume no greater than 50 ml. To this aliquot in a beaker add permanganate solution (2–3 drops) until a pink color remains. Heat for 25 min. Add more permanganate solution if the pink color fades. Then add 5% (w/v) potassium bromide solution until the pink color disappears; add 3 drops in excess. Boil for 5 min. Cool and transfer to 50-ml volumetric flasks. Add 1 ml of *s*-diphenylcarbazide solution, dilute to volume with water, and let stand for 5 min. The color is stable for 1 h.

Prepare a blank by taking a similar aliquot of the acid and water used in dissolution of the sample and follow the procedure described for the color development of the sample.

Determine the optical densities of the blank and samples on a Beckman DU Spectrophotometer with 5-cm cells at a wavelength of 545 mμ with water in the reference cell. After the average optical density of the blank has been subtracted from that of the samples, the corrected optical densities are compared to a standard curve obtained with 0.5–10 μg of chromium. Results are shown in Table VI.

* Aliquots should contain no more than 0.10 g of beryllium and should be adjusted to a volume of 25 ml with a nitric acid solution of pH 1. For a blank use 25 ml of this nitric acid solution.

TABLE VI

CHROMIUM BY THE DIPHENYLCARBAZIDE METHOD

Cr (μg)	*Distilled Be (mg)*	*O.D.*	*O.D. minus average blank*	*O.D. per μg Cr*
0.0	0	0.010		
	0	0.011		
2.5	0	0.205	0.195	0.0780
	0	0.207	0.197	0.0788
5.0	0	0.405	0.395	0.0790
	0	0.400	0.390	0.0780
10.0	0	0.800	0.790	0.0790
	0	0.795	0.785	0.0785
0.0	192	0.308		
	192	0.304		
5.0	192	0.700	0.394[a]	0.0788
	192	0.703	0.397[a]	0.0794

[a] Minus average O.D. for unspiked beryllium samples.

THE DETERMINATION OF MANGANESE[8]

Reagents

PAN solution (0.1%). Dissolve 1 g of PAN in 100 ml of methanol.

Buffer solution. Dissolve 10 g of sodium citrate and 5 g of ammonium chloride in 100 ml of water.

Procedure

After dissolution of the sample as described for the determination of chromium, a stock solution is made up such that aliquots can be taken to contain 0.10 g of sample

TABLE VII

MANGANESE BY THE PAN METHOD

Mn (μg)	*Distilled Be (mg)*	*O.D.*	*O.D. minus average blank*	*O.D. per μg Mn*
0.0	0	0.048		
	0	0.049		
1.0	0	0.155	0.107	0.107
	0	0.162	0.114	0.114
2.5	0	0.310	0.262	0.105
	0	0.318	0.270	0.108
5.0	0	0.600	0.552	0.110
	0	0.609	0.561	0.112
0.0	109.7	0.128		
	109.7	0.130		
1.0	109.7	0.242	0.113[a]	0.113
	109.7	0.239	0.110[a]	0.110
2.5	109.7	0.418	0.289[a]	0.116
	109.7	0.420	0.291[a]	0.116
5.0	109.7	0.710	0.581[a]	0.116
	109.7	0.715	0.586[a]	0.117

[a] Minus average O.D. for unspiked beryllium samples.

in a volume no greater than 25 ml. Transfer the aliquot to a 125-ml separatory funnel and add 10 ml of buffer solution. Add 2 ml of 0.1 *N* potassium cyanide solution and mix. Pipette in 1 ml of PAN solution and set the timer for 1 min. Immediately add 5 ml of concentrated ammonium hydroxide and mix. After 1 min has elapsed, add 10 ml of chloroform and shake for 40 sec. Drain the chloroform layer into a dry 25-ml volumetric flask. Add a second 10 ml portion of chloroform and shake for 40 sec. Drain into the same volumetric flask. Dilute to volume with chloroform.

Prepare a blank by taking a similar aliquot of the acid and water used in dissolution of the sample and follow the procedure described for the color development and extraction of the sample.

Prepare a standard curve by following the procedure used for sample preparation on aliquots containing 0.10 g of Pechiney super-purity flake beryllium* (obtained from General Astrometals Corporation, Yonkers, New York) and 1–5 μg of manganese. The curve obtained with beryllium present is slightly more sensitive than that obtained in absence of beryllium (Table VII). This may be due to a neutralization of the inhibiting effect of the citrate because of the formation of the beryllium citrate complex. Therefore, the curve is prepared from solutions containing 0.100 $\pm$ 0.010 g of beryllium.

Determine the optical densities of the blank and samples on a Beckman DU Spectrophotometer with 5-cm cells at a wavelength of 560 mμ with water in the reference cell. After the average optical density of the blank has been deducted from that of the samples, the corrected optical densities are compared to a standard curve obtained with 1–5 μg of manganese and 0.10 g of beryllium.

CONCLUSIONS

Wet chemical methods have been established for the determination of several trace impurities in very high-purity beryllium. These techniques have furnished reliable analytical data for the analysis of distilled beryllium and provide absolute values of high sensitivity. The methods can be performed readily and require no instrumentation other than a spectrophotometer. Comparative data obtained in different laboratories are shown in Table VIII.

TABLE VIII

COMPARISON OF NUCLEAR METALS, INC. AND GENERAL ASTROMETALS, INC. ANALYSES ON SEVERAL BATCHES OF PECHINEY FLAKE (SUPPLIED BY GENERAL ASTROMETALS, INC.)

Pechiney flake	*Analysis performed at*	*Fe (p.p.m.)*	*Ni (p.p.m.)*	*Cu (p.p.m.)*	*Al (p.p.m.)*	*Si (p.p.m.)*	*Cr (p.p.m.)*	*Mn (p.p.m.)*
Regular	Nuclear Metals	160 142	128 130 116	85	75 55	9 9	19 12	15 20
	General Astrometals	140 170	95	100	50	<15 20	10 10	15
Super pure	Nuclear Metals	43	6		20	5 4 7		9
	General Astrometals	19	31 15	<5 <5	<50 <50	<10 <10	<5 <5	11 15

* A typical manganese analysis reported by the supplier is 20 p.p.m.

Comparable data on distilled beryllium obtained by mass spectrometry, emission spectrography and activation analysis are sparse. Even if these techniques are further developed, reliable standards will be needed. Wet chemical methods of analysis will be most useful in providing standards for these instrumental techniques.

SUMMARY

Photometric methods for the analysis of iron, nickel, copper, aluminum, silicon, chromium and manganese in high-purity beryllium are described.

RÉSUMÉ

Les auteurs décrivent une méthode pour le dosage photométrique de traces de fer, de nickel, de cuivre, d'aluminium, de silicium, de chrome et de manganèse dans un béryllium de grande pureté.

ZUSAMMENFASSUNG

Beschreibung von photometrischen Methoden zur Bestimmung von Spuren von Eisen, Nickel, Kupfer, Aluminium, Silizium, Chrom und Mangan in hochreinem Beryllium.

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A COMPLEXIMETRIC METHOD FOR THE DETERMINATION OF DISSOLVED OXYGEN IN WATER

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Of the titrimetric methods available for the determination of dissolved oxygen in water, the method of WINKLER[1] is most widely applied[2,3]. For use on board ship or in the field it has, however, several disadvantages such as the corrosiveness of the reagents, the elaborate precautions needed for work with polluted water, and the instability of the thiosulfate titrant. The solutions of ferrous salts and of ascorbic acid used in other methods[4-7] are even more unstable.

In the method proposed here, the reagents used are neither corrosive nor hygroscopic and they may be applied in solid form. EDTA is the titrant, so that frequent restandardizations are unnecessary[8]. The chemical reactions taking place during the determination can be summarized as follows: dissolved oxygen reacts with iron(II) to form iron(III) which is then titrated with EDTA solution in presence of salicylic acid as indicator. The difference between the stability constants of the iron(II) and iron(III) chelates of salicylic acid[9,10] is greater than the corresponding difference between the sulfosalicylic compounds, hence salicylic acid is more suitable for the titration of iron(III) in the presence of iron(II). Other iron indicators such as tiron and eriochrome azurol S are less convenient, because of slow reactions in cold solution[8].

The rate of the reaction of oxygen with iron(II) is strongly dependent on pH. It was found that under the conditions prevailing during the determination, it is complete within seconds above pH 7 but takes days below pH 3. A pH of 7.5 was chosen; at higher pH iron hydroxides precipitate, and do not dissolve immediately after addition of acid, so that titrations tend to drag. For the same reason — to avoid precipitation — ferrous ethylenediamine sulfate (FES) is preferable to Mohr's salt as the source of iron(II). A pH of 2.4 was chosen for the titration stage, not only to avoid interference by atmospheric oxygen, calcium, magnesium and iron(II), but also because at this pH the violet 1:1 ferric salicylate chelate predominates and a sharper end-point is obtained from violet to the bright yellow-green of the iron(III)–EDTA chelate. For the pH adjustment, tris(hydroxymethyl)aminomethane (THAM) and maleic acid were chosen; these do not cause precipitation and are convenient to handle. The buffering capacity of the test solution is considerable and no harm is done if not exactly the proper amounts of THAM and maleic acid are added.

During the reaction of dissolved oxygen with iron(II) the sample should be sealed off from the air; the conventional WINKLER technique may be applied. The data

presented here were obtained with wide-necked bottles, the necks of which provided enough space to carry out the titration in the bottles themselves. As soon as the glass stopper is removed the liquid must be acidified to stop the reaction with oxygen. Air interference during the admixture of the maleic acid can be avoided in various ways. For field use, 0.3% of glyceryl monostearate can be added to the solid maleic acid; this makes it float for a moment before dissolution so that the liquid is sealed off by an acidic layer. For laboratory use the application of an alcoholic instead of an aqueous solution serves the same purpose.

EXPERIMENTAL

Ferrous ethylenediamine sulfate. This must not contain iron(III). (To check this, add to boiling water some sodium salicylate, maleic acid and FES; no violet color should develop.) Preparations containing iron(III) are difficult to purify by recrystallization. Better results can be obtained as follows. Prepare a concentrated solution of the impure salt in *slightly* acidic water, filter if necessary, and add some salicylate and sufficient EDTA solution just to remove the violet color. Precipitate with an equal volume of ethanol, filter by suction, wash with ethanol and dry in a stream of cold dry air.

Procedure

To a sample of water in a weighed glass-stoppered bottle of volume about 100 ml add in the following order, 2 ml of aqueous 15% sodium salicylate solution (or 250–300 mg of solid), 150–200 mg of FES and 0.5 ml of aqueous 20% THAM solution (or 80–120 mg of solid). Immediately close the bottle, without enclosing air bubbles, and mix by thorough shaking. (The intensity of the brown color of the 1:2 ferric salicylate chelate gives a rough idea of the amount of dissolved oxygen in the water.) Open the bottle and immediately add 5 ml of an ethanolic 15% solution of maleic acid (for field use, use 600–900 mg of a mixture of maleic acid ground with 0.3% glyceryl monostearate in a mortar). The color changes to a deep violet. Titrate with 0.02 *M* EDTA solution (disodium salt) until the last trace of violet has disappeared from the yellow-green color of the ferric–EDTA chelate.

RESULTS AND DISCUSSION

Under comparable conditions concerning the human and the equipment factors, the

TABLE I

REPLICATE DETERMINATIONS IN ONE BATCH OF AGED IJMUIDEN TAP WATER

(Ca^{2+} 5.0, Mg^{2+} 1.3, HCO_3^- 5.1 meq/l)

	Unmodified Winkler procedure[2] *(mg O_2/l)*	*Complexometric method (mg O_2/l)*
	9.36	9.45
	9.44	9.43
	9.38	9.30
	9.41	9.34
	9.47	9.39
Average	9.41	9.38
Standard deviation	0.045	0.062

precision of the complexiметric method for unpolluted water was found to be less than that of the unmodified WINKLER procedure (Table I). The sharper color change of a good starch indicator compared with the more gradual fading of the ferric salicylate color is probably the cause.

The accuracy of both methods is the same for unpolluted water and no significant differences were obtained. The data given in Table II suggest that in the case of a

TABLE II

ERRORS CAUSED BY ADDED INTERFERING SUBSTANCES[a]

Substance added	*(mg/l)*	*Deviations (mg O_2/l)*	
		Unmodified Winkler procedure[a]	*Complexi-metric method*
NO_2^-	10	+ 4.7	0.0
NO_2^-	100	> + 50	+ 3.1
SO_3^{2-}	10	− 0.3	0.0
SO_3^{2-}	100	− 1.2	0.0
$S_2O_3^{2-}$	10	− 0.6	0.0
$S_2O_3^{2-}$	100	− 2.8	0.0
Dextrose	100	− 0.4	0.0
Fermented potato[b]	1[c]	− 0.9	− 0.2
Fermented potato[b]	5[c]	− 1.7	− 0.5
Ascorbic acid	50	− 6.2	− 2.2
Ascorbic acid	100	> − 10	− 4.7
PO_4^{3-}	5	0.0	0.0
Cl (added as NaOCl)	4.5	+ 0.8	0.0
Fe^{3+}			interferes[d]

[a] The water used was aged IJmuiden tap water (Ca^{2+} 5.0, Mg^{2+} 1.3, HCO_3^- 5.1 meq/l).
[b] Sliced raw potato with water (1:3) was incubated for 4 days at 37°, and was highly decomposed by butyric acid bacteria *(Clostridium pectinovorum)*.
[c] Ml of filtrate of broth added per 100 ml of tap water.
[d] See text.

water containing significant amounts of unknown substances, the complexiметric method should give more accurate results. However, the possibility of a reaction between these unknown substances and free dissolved oxygen taking place *during* the determination always remains.

As shown in Table II the proposed method is less sensitive to interfering substances than the unmodified WINKLER procedure. Iron(III) interferes, of course, but the presence of iron(III) hydroxide has hardly any effect; it was shown that when a millimolar suspension of iron(III) hydroxide (made by aerating a ferrous bicarbonate solution) was mixed with maleic acid and salicylate as used in the test, only 2% was dissolved in 1 h. Much depends therefore on the state in which the iron(III) is present; with iron-containing waters it is advisable to carry out two determinations — one with and one without addition of FES and THAM — and to subtract the results.

The lack of interference from halogens is apparently caused by substitution reactions in the sodium salicylate, for a strong smell of the iodoform type develops

on addition of sodium salicylate to samples containing free chlorine or iodine. The substitution of sea water for fresh water has no effect on the accuracy and precision of the method.

SUMMARY

A new method is proposed for the determination of dissolved oxygen in water. The iron(III) formed from FES at pH 7.5 is titrated with EDTA solution in presence of salicylic acid indicator after adjustment of the pH to about 2.4 The method is slightly less precise than the WINKLER method for pure waters but more accurate for polluted waters; it is simple and convenient for field use.

RÉSUMÉ

Une nouvelle méthode est proposée pour le dosage de l'oxygène dissous dans l'eau. Elle est basée sur l'oxydation du sulfate de fer(II)–éthylènediamine par l'oxygène dissous; le fer(III) formé est titré par l'EDTA, en présence d'acide salicylique comme indicateur.

ZUSAMMENFASSUNG

Es wird eine einfache Methode beschrieben zur Bestimmung von gelöstem Sauerstoff in Wasser. Sie beruht auf der Oxydation von Eisen-(II)–Äthylendiaminsulfat (FES) durch den gelösten Sauerstoff und Titration des Eisen-(III) mit EDTA und Salicylsäure als Indikator.

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MICROHETEROMETRIC TITRATIONS OF LARGE ORGANIC NITROGEN-CONTAINING COMPOUNDS AND OF HETEROPOLY ACIDS

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The determination of large organic nitrogen compounds, especially of alkaloids, with heteropoly acids has already been studied by many workers[1]. The high molecular weight of the acids makes them suitable reagents for the gravimetric determination of alkaloids; the precipitates obtained are generally determined either by gravimetry or by nephelometry. Special attention has been paid to the elaboration of methods for the determination of quinine or nicotine. In the latter case, a correction must be made for the solubility of the precipitate in hydrochloric acid of various concentrations. SPIES[1] dried the precipitate obtained from nicotine at 650°. KYKER AND LEWIS[1] determined alkaloids and other bases by photometric turbidity. However, difficulties arose in the extraction of the bases, which was lengthy. For example, quinine was troublesome to extract from blood; the extraction took many hours and the error was sometimes equal to 50%. Another difficulty was found in obtaining appropriate and stable standards. Colorimetric and nephelometric methods have been used, but some authors believe that for directness, accuracy and ease of manipulation, the precipitation and gravimetric determination as silicotungstate is preferable. However, many workers suggest that the precipitation method with heteropoly acids is unreliable, the composition of the complexes being uncertain and occlusion of extraneous matter likely. They therefore prefer preliminary separation and solvent extraction after liberation of the alkaloid though such extractions are lengthy and unreliable; the extracted alkaloid complex is then dissolved in acid, excess of which is back-titrated with alkali in the presence of a suitable indicator. In all cases of precipitation of an alkaloid a large excess of heteropoly acid was necessary.

It seemed to us that the heterometric determination of both the alkaloid, and reversely of the heteropoly acid, might be advantageous compared with the above-mentioned methods. Heterometry[2] is completely independent of occlusions, whatever they may be. The solubility of the precipitates obtained, whatever the acid concentration, has no effect on the precision of the results in heterometry. Standard curves which are unreproducible are not used. No troublesome and unreliable extractions are necessary.

In the present paper a method is described for the direct titration of nitrogen compounds in acidic solution with heteropoly acids. Although similar titrations with tetraphenylborate[3] are often 3 to 6 times more sensitive, nevertheless the titrations

with heteropoly acids are precise, generally giving negligible errors. Moreover, when silicotungstic acid is used as the titrant, nitrogen compounds can be titrated at pH values of about 1 and 7, and valuable additional quantitative information about the character of the nitrogen atoms in the alkaloid can be obtained. Probably these titrations could be used to analyse mixtures of nitrogen compounds and to determine each compound in the presence of the rest.

Moreover the technique provides a sensitive and precise method for the direct determination of heteropoly acids (2.5–5 ml of 10^{-4} *M* acid), with a nitrogen compound as titrant.

In most cases, the titration time is 7 to 15 min.

EXPERIMENTAL

Instrumentation

The instrumentation and working conditions have been described previously[2].

Chemicals

The nitrogen-containing compounds were the same as those used in the previous work with alkaloids[3].

Silicotungstic acid. $SiO_2 \cdot 12WO_3 \cdot 24H_2O$, Baker Analyzed Reagent.

Phosphomolybdic acid. $H_3PO_4 \cdot 12MoO_3 \cdot 24H_2O$, Hopkin & Williams Ltd., analytical reagent.

Phosphotungstic acid. $P_2O_5 \cdot 24WO_3 \cdot mH_2O$, Baker Analyzed Reagent.

Procedure

(1) *Determination of nitrogen compounds.* 20 ml of 0.001–0.002 *M* solution of an alkaloid or other large organic nitrogen-containing compound, containing 1 ml of *M* hydrochloric acid (or 2 ml of *M* sodium acetate) were titrated heterometrically with a 0.00125–0.005 *M* solution of heteropoly acid.

(2) *Determination of heteropoly acids.* 20 ml of 0.00025–0.0005 *M* silicotungstic, phosphotungstic or phosphomolybdic acid containing 1 ml of *M* hydrochloric acid (or 2 ml of *M* sodium acetate) were titrated heterometrically with a 0.01–0.00025 *M* solution of a large nitrogen compound.

RESULTS AND DISCUSSION

Titration of nitrogen compounds with heteropoly acids

A selection of titrations of alkaloids or other large nitrogen-containing compounds with heteropoly acids is given in Table I. The graphs of some of these titrations are shown in Fig. 1. Each compound was titrated with three different heteropoly acids. In the case of morphine, the titrations were successful only when phosphotungstic acid was used as titrant; titrations of nicotine with phosphomolybdic acid proved impossible. At the beginning of this investigation many titrations with all three acids were carried out at pH *ca.* 7. The titrations were always clear and the results were strictly reproducible, only when silicotungstic acid was used. The results of titrations with the different acids at pH *ca.* 3 and pH *ca.* 5 have been omitted from the Tables; at these pH values many successful titrations were carried out with all three acids. This is in contrast to the results obtained at pH *ca.* 7.

The mineral acid content of the analysed solutions was not critical when the less soluble nitrogen–heteropoly compounds were used. The solution contained 1 or 5 ml of *N* hydrochloric acid in 20 ml of solution. With 5 ml of acid, the maximum density

TABLE

TITRATION OF SOME NITROGEN-CONTAINING

General composition: *a* ml nitrogen compound (A) + *b* ml supplements + ad 20 ml H_2O + *x* ml hetero
HP = hetero

Exp. No.	*Titrated solution*	*Titrant*	
		Name	*Molarity*
1	4 ml 0.01 *M* nitron + 1 ml *M* HCl	Silicotungstic acid	0.0025
2	4 ml 0.01 *M* nitron + 2 ml *M* NaAc	Silicotungstic acid	0.0025
3	3 ml 0.005 *M* nitron + 1 ml *M* HCl	Phosphomolybdic acid	0.00125
4	3 ml 0.01 *M* nitron + 1 ml *M* HCl	Phosphotungstic acid	0.0025
5	3 ml 0.01 *M* quinine + 1 ml *M* HCl	Silicotungstic acid	0.005
6	3 ml 0.01 *M* quinine + 5 ml *M* HCl	Silicotungstic acid	0.005
7	3 ml 0.005 *M* quinine + 2 ml *M* NaAc	Silicotungstic acid	0.00125
8	3 ml 0.0025 *M* quinine + 2 ml *M* NaAc	Silicotungstic acid	0.00125
9	3 ml 0.01 *M* quinine + 1 ml *M* HCl	Phosphomolybdic acid	0.005
10	3 ml 0.01 *M* quinine + 1 ml *M* HCl	Phosphotungstic acid	0.005
11	4 ml 0.01 *M* strychnine + 1 ml *M* HCl	Silicotungstic acid	0.0025
12	4 ml 0.01 *M* strychnine + 2 ml *M* NaAc	Silicotungstic acid	0.0025
13	3 ml 0.01 *M* strychnine + 1 ml *M* HCl	Phosphomolybdic acid	0.0025
14	3 ml 0.01 *M* strychnine + 1 ml *M* HCl	Phosphotungstic acid	0.0025
15	4 ml 0.01 *M* papaverine + 1 ml *M* HCl	Silicotungstic acid	0.0025
16	3 ml 0.01 *M* papaverine + 2 ml *M* NaAc	Silicotungstic acid	0.0025
17	3 ml 0.01 *M* papaverine + 1 ml *M* HCl	Phosphomolybdic acid	0.0025
18	3 ml 0.01 *M* yohimbine + 1 ml *M* HCl	Silicotungstic acid	0.0025
19	3 ml 0.01 *M* yohimbine + 2 ml *M* NaAc	Silicotungstic acid	0.0025
20	3 ml 0.01 *M* yohimbine + 1 ml *M* HCl	Phosphomolybdic acid	0.0025
21	3 ml 0.01 *M* yohimbine + 1 ml *M* HCl	Phosphotungstic acid	0.0025
22	3 ml 0.0025 *M* nicotine + 1 ml *M* HCl	Silicotungstic acid	0.00125
23	3 ml 0.005 *M* nicotine + 2 ml *M* NaAc	Silicotungstic acid	0.0025
24	3 ml 0.0025 *M* nicotine + 5 ml *M* HCl	Phosphotungstic acid	0.00125
25	3 ml 0.005 *M* atropine + 1 ml *M* HCl	Silicotungstic acid	0.00125
26	3 ml 0.01 *M* atropine + 1 ml *M* HCl	Phosphomolybdic acid	0.0025
27	3 ml 0.005 *M* atropine + 1 ml *M* HCl	Phosphotungstic acid	0.00125
28	3 ml 0.0025 *M* atropine + 1 ml *M* HCl	Phosphotungstic acid	0.000625
29	3 ml 0.005 *M* morphine + 1 ml *M* HCl	Phosphotungstic acid	0.0025
30	4 ml 0.0025 *M* phenanthroline + 1 ml *M* HCl	Silicotungstic acid	0.000625
31	4 ml 0.01 *M* phenanthroline + 2 ml *M* NaAc	Silicotungstic acid	0.00125
32	3 ml 0.01 *M* phenanthroline + 1 ml *M* HCl	Phosphotungstic acid	0.0025

values achieved were slightly higher than those obtained with 1 ml. The influence of the acidity of the solution (pH *ca.* 1 or pH *ca.* 7) is different if the organic molecule contains one or two active heterocyclic nitrogen atoms. Thus, quinine, phenanthroline and nicotine have two active nitrogen atoms in the molecule. With both quinine and phenanthroline, twice the number of base molecules to each molecule of silicotungstic acid was bound at pH *ca.* 7 compared to the amount bound at pH 1; but in the case of nicotine, no precipitation at all occurred at pH 7. In the titration of phenanthroline with silicotungstic acid at pH *ca.* 1, both nitrogen atoms of the phenanthroline molecule were involved in the formation of a monovalent cation, the final compound

I

COMPOUNDS WITH HETEROPOLY ACIDS

poly acid (HP) (T = 20°) (i = intersection point; h = horizontal maximum density line; A = alkaloid; poly acid)

End-point			Error (%)	Intermediate compounds [A]:[HP]	Titration time (min)
Found (ml)	Optical density	Molar ratios [A]:[HP]			
i 4.00 h	0.70	4 : 1	0.0	8 : 1	9
i 4.05 h	0.74	4 : 1	1.3		7
i 4.00 h	0.76	3 : 1	0.0		12
i 4.00 h	0.51	3 : 1	0.0	~6 : 1 ↓	9
i 3.05 h	0.62	2 : 1	1.7		15
i 3.00 h	0.84	2 : 1	0.0	4 : 1 ↓	14
i 3.1 h	0.85	4 : 1	7.0	6 : 1 ↓	8
i 1.5 h	0.73	4 : 1	0.0		5
i 4.00 h	0.96	3 : 2	0.0	4 : 1 ↓ → 2 : 1 ↓	10
i 4.00	0.65	3 : 2	0.0	2 : 1 ↓	15
i 4.00 h	0.79	4 : 1	0.0	8 : 1 ↓	25
i 4.00 h	0.71	4 : 1	0.0	8 : 1 ↓	20
i 3.97 h	0.96	3 : 1	0.75	8 : 1 ↓	15
i 4.00 h	0.73	3 : 1	0.0	8 : 1 ↓	11
i 4.05 h	0.45	4 : 1	1.25		9
i 3.00 h	0.49	4 : 1	0.0	6 : 1 ↓ → 5 : 1 ↓	8
i 3.93 h	0.68	3 : 1	1.8	7 : 1 ↓ → 4 : 1 ↓	10
i 3.00 h	0.78	4 : 1	0.0	~5 : 1 ↓	12
i 2.97 h	0.88	4 : 1	1.0	~8 : 1 ↓	6
i 4.2 h	1.07	3 : 1	5.0	6 : 1 ↓ → 4 : 1 ↓	13
i 4.00 h	0.90	3 : 1	0.0		10
i 3.00 h	0.82	2 : 1	0.0	8 : 1 ↓ → 4 : 1 ↓ → 3 : 1 ↓	8
	No ppt.				10
i 3.9 h	0.87	3 : 2	2.5	6 : 1 ↓ → ~ 3 : 1 ↓ → 2 : 1 ↓	10
2.7(?) h	0.90	4 : 1	10.0		12
i 4.0 h	1.03	3 : 1	0.0	12 : 1 ↓ → 7 : 1 ↓ → 6 : 1 ↓	25
i 3.97 h	0.84	3 : 1	0.8		7
i 4.00 h	0.75	3 : 1	0.0	~ 4.5 : 1 ↓	20
i 2.0 h	0.85	3 : 1	0.0	6 : 1 ↓ → 4 : 1 ↓	12
i 4.00 h	0.78	4 : 1	0.0	8 : 1 ↓	8
i 4.00 h	0.85	8 : 1	0.0	16 : 1 ↓ → 12 : 1 ↓	10
i 4.00 h	0.78	3 : 1	0.0		15

obtained being Ph_4SiW_1. At pH *ca.* 7, two phenanthroline molecules somehow acted as a monovalent unit (Ph_8SiW_1).

With quinine, two nitrogen atoms were active at pH *ca.* 1, while at pH *ca.* 7 only one nitrogen atom was active in the molecule. Remarkably, the sensitivity of the quinine titration at pH *ca.* 7 was almost four-fold that at pH *ca.* 1, and the titration was even faster at pH 7. In the case of phenanthroline, the opposite happened. In all other cases, where only one nitrogen atom was active in the molecule, the results of the titrations were similar at both pH values and the titrations were of the same sensitivity.

Because of the solubility of the nicotine compound, no analogous study could be carried out at pH 7 with this alkaloid. On the other hand, with both yohimbine and strychnine, only one nitrogen atom reacted at pH values of 1–7; the final compounds, Yo_4SiW_1 and Str_4SiW_1, were always obtained. The examples given show how the study of large and complex nitrogen-containing compounds can assist in their classification according to the behaviour of their nitrogen atoms.

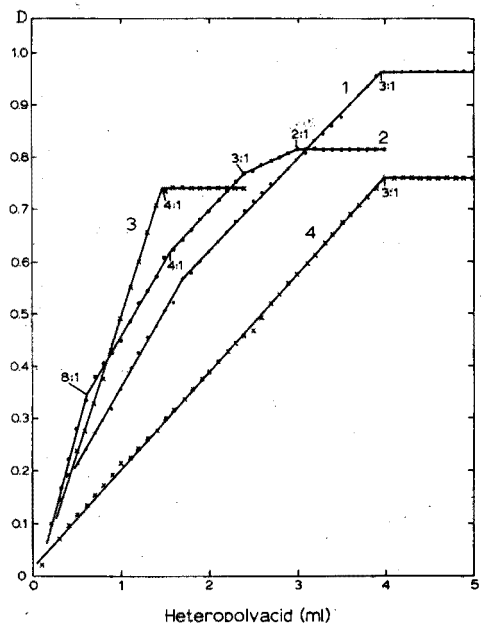

Fig. 1. 1. (Table I, 13) 3 ml 0.01 *M* strychnine + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.0025 *M* phosphomolybdic acid. 2. (Table I, 22) 3 ml 0.0025 *M* nicotine + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.00125 *M* silicotungstic acid. 3. (Table I, 8) 3 ml 0.0025 *M* quinine + 2 ml *M* Na-acetate + 15 ml H_2O + *x* ml 0.00125 *M* silicotungstic acid. 4. (Table I, 3) 3 ml 0.005 *M* nitron + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.00125 *M* phosphomolybdic acid.

In the analysis of mixtures of alkaloids or other large nitrogen-containing compounds, simultaneous titrations at pH *ca.* 1 and pH *ca.* 7 with silicotungstic acid may often make possible the analysis of two or perhaps more nitrogen compounds without previous separations. The analysed compounds may be insoluble both at pH 1 and pH 7. The single compounds may then be derived from the intermediates and from the final end-points obtained at the two pH values. The compounds may all be insoluble at pH 1, while some may be soluble at pH 7. All these possibilities can be evaluated by heterometry.

Silicotungstic acid seems to be specially adapted for such studies and analyses. If the behaviour of this acid is compared with the behaviour of tetraphenylborate, which can be used[2,3] even at pH 9 and which behaves similarly to some degree, it can be seen that silicotungstic acid offers a larger variety of such possibilities, owing to its more complex structure.

To allow a comparison of the sensitivities of the titrations of various nitrogen-

containing compounds with heteropoly acids, Table II shows the molarity of one ml of nitrogen compound which was necessary in each case to obtain at pH *ca.* 1 a maximum density value of 0.7 to 1.0. From Table II it can be concluded that high

TABLE II

SENSITIVITY OF TITRATIONS

N-compound (1 ml in 20 ml soln.)		*Titrated with*		
Name	*Molarity*	*Silicotungstic*	*Phosphomolybdic*	*Phosphotungstic*
Nicotine	0.0075	+		+
Quinine (pH 7)	0.0075	+		
Phenanthroline	0.01	+		
Atropine	0.015	+	+	+
Nitron	0.015		+	
Morphine	0.015			+
Quinine (pH 1)	0.03	+	+	+
Yohimbine	0.03	+	+	+
Phenanthroline	0.03			+
Strychnine	0.03		+	+
Papaverine	0.03		+	
Nitron	0.03			+
Nitron	0.04	+		
Strychnine	0.04	+		
Papaverine	0.04	+		

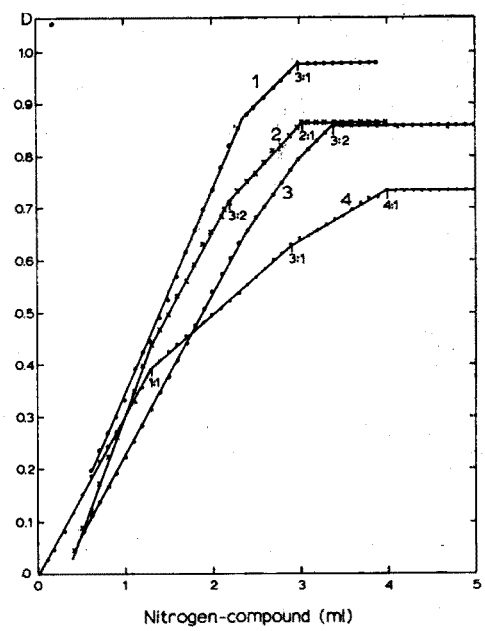

Fig. 2. 1. (Table III, 15) 4 ml 0.0025 *M* phosphomolybdic acid + 1 ml *M* HCl + 15 ml H_2O + *x* ml 0.01 *M* papaverine. 2. (Table III, 21) 3 ml 0.00125 *M* silicotungstic acid + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.0025 *M* nicotine. 3. (Table III, 7) 3 ml 0.0025 *M* phosphomolybdic acid + 1 ml *M* HCl + 16 ml H_2O + *x* ml 0.0033 *M* quinine. 4. (Table III, 24) 4 ml 0.00125 *M* silicotungstic acid + 5 ml *M* HCl + 11 ml H_2O + *x* ml 0.005 *M* phenanthroline.

TABI

TITRATION OF SOME HETEROPOLY ACI

General composition: a ml heteropoly acid (HP) + b ml supplements + ad 20 ml H_2O + x ml nitrog
HP = hete

Exp. No.	*Titrated solution*	*Titrant*	
		Name	*Molarity*
1	4 ml 0.00125 *M* Silicotungstic acid + 1 ml *M* HCl	nitron	0.005
2	4 ml 0.00125 *M* Silicotungstic acid + 2 ml *M* NaAc	nitron	0.005
3	4 ml 0.00125 *M* Phosphomolybdic acid + 5 ml *M* HCl	nitron	0.005
4	4 ml 0.0025 *M* Phosphotungstic acid + 1 ml *M* HCl	nitron	0.01
5	3 ml 0.005 *M* Silicotungstic acid + 1 ml *M* HCl	quinine	0.01
6	3 ml 0.0025 *M* Silicotungstic acid + 2 ml *M* NaAc	quinine	0.01
7	3 ml 0.0025 *M* Phosphomolybdic acid + 1 ml *M* HCl	quinine	0.0033
8	4 ml 0.005 *M* Phosphotungstic acid + 1 ml *M* HCl	quinine	0.01
9	4 ml 0.0025 *M* Silicotungstic acid + 1 ml *M* HCl	strychnine	0.01
10	4 ml 0.0025 *M* Silicotungstic acid + 2 ml *M* NaAc	strychnine	0.01
11	4 ml 0.00125 *M* Phosphomolybdic acid + 1 ml *M* HCl	strychnine	0.005
12	4 ml 0.0025 *M* Phosphotungstic acid + 1 ml *M* HCl	strychnine	0.01
13	4 ml 0.0025 *M* Silicotungstic acid + 1 ml *M* HCl	papaverine	0.01
14	4 ml 0.0025 *M* Silicotungstic acid + 2 ml *M* NaAc	papaverine	0.01
15	4 ml 0.0025 *M* Phosphomolybdic acid + 1 ml *M* HCl	papaverine	0.01
16	6 ml 0.0025 *M* Phosphotungstic acid + 1 ml *M* HCl	papaverine	0.01
17	3 ml 0.0025 *M* Silicotungstic acid + 1 ml *M* HCl	yohimbine	0.01
18	3 ml 0.0025 *M* Silicotungstic acid + 2 ml *M* NaAc	yohimbine	0.01
19	4 ml 0.00125 *M* Phosphomolybdic acid + 1 ml *M* HCl	yohimbine	0.005
20	4 ml 0.0025 *M* Phosphotungstic acid + 1 ml *M* HCl	yohimbine	0.01
21	3 ml 0.00125 *M* Silicotungstic acid + 1 ml *M* HCl	nicotine	0.0025
22	3 ml 0.00125 *M* Silicotungstic acid + 1 ml *M* NaAc	nicotine	0.0025
23	4 ml 0.00125 *M* Phosphotungstic acid + 5 ml *M* HCl	nicotine	0.0025
24	4 ml 0.00125 *M* Silicotungstic acid + 5 ml *M* HCl	phenanthroline	0.005
25	4 ml 0.00125 *M* Phosphomolybdic acid + 1 ml *M* HCl	phenanthroline	0.005
26	4 ml 0.0025 *M* Phosphotungstic acid + 1 ml *M* HCl	phenanthroline	0.01

sensitivity (0.0075 *M* to 0.015 *M*) is obtained in special cases with silicotungstic acid. A sensitivity of 0.03 *M* to 0.04 *M* is obtained with all the heteropoly acids and with most nitrogen compounds. Even at the maximum sensitivity, the titrations with silicotungstic acid are still 2 to 3 times less sensitive than those with tetraphenylborate. In most other cases the sensitivity of the titrations with heteropoly acids is about 5 to 6 times less than that obtainable with tetraphenylborate. Nevertheless, the titrations with heteropoly acids can supply additional information of a general and analytical nature which cannot be obtained from other titrations.

Titrations of heteropoly acids with large nitrogen compounds

Table III presents a selection of such titrations. The course of some titrations is presented in Fig. 2. It can be seen that all the heteropoly acids can be successfully determined in concentrations of $2.5 \cdot 10^{-4}$ *M* to $5 \cdot 10^{-4}$ *M* with any of the nitrogen compounds mentioned; the error is generally near zero.

NITROGEN-CONTAINING COMPOUNDS

pound (A) (T = 20°) (i = intersection point; h = horizontal maximum density line; A = alkaloid; acid)

End-point			Error (%)	Intermediate compounds [A]:[HP]	Titration time (min)
Found (ml)	Optical density	Molar ratios [A]:[HP]			
i 4.00 h	0.60	4 : 1	0.0	~ 1 : 1 ↓ → ~ 3 : 1 ↓	10
i 4.00 h	0.50	4 : 1	0.0	1 : 1 ↓ → 3 : 1 ↓	13
i 3.00 h	0.75	3 : 1	0.0	~ 1 : 1 ↓	15
i 3.00 h	0.60	3 : 1	0.0		15
i 3.00 h	0.75	2 : 1	0.0	3 : 2 ↓	9
i 2.5 h	0.91	3 : 1			6
i 3.33 h	0.85	3 : 2	1.5		10
i 3.00 h	0.72	3 : 2	0.0	1 : 1 ↓	9
i 4.00 h	0.96	4 : 1	0.0		9
i 4.00 h	0.90	4 : 1	0.0	2 : 1 ↓	9
i 2.97 h	0.95	3 : 1	1.0	3 : 2 ↓	11
i 3.00 h	0.80	3 : 1	0.0		7
i 4.00 h	0.57	4 : 1	0.0	5 : 2 ↓ → ~ 3 : 1 ↓	8
i 4.00 h	0.62	4 : 1	0.0	~3 : 1 ↓	9
i 3.0 h	0.97	3 : 1	0.0		17
i 4.5 h	0.59	3 : 1	0.0	~2 : 1 ↓	13
i 3.00 h	0.80	4 : 1	0.0		13
i 3.00 h	0.79	4 : 1	0.0	1 : 1 ↓ → 5 : 2 ↓	11
i 3.00 h	0.85	3 : 1	0.0	~2 : 1 ↓	13
i 3.00 h	0.98	3 : 1	0.0	1 : 1 ↓ → ~ 5 : 2 ↓	14
i 3.00 h	0.85 No ppt.	2 : 1	0.0	~ 1 : 1 ↓ → 3 : 2 ↓	12
i 3.00 h	0.82	2 : 3	0.0	1 : 2 ↓ → 3 : 4 ↓	7
i 4.00 h	0.73	4 : 1	0.0	~ 1 : 1 ↓ → 3 : 1 ↓	9
i 3.00 h	0.85	3 : 1	0.0	~3 : 2 ↓	13
i 3.00 h	0.85	3 : 1	0.0	2 : 1 ↓	8

The importance of these titrations lies in the possibility of using these reactions for the determination of minute quantities of phosphorus or silicon after conversion of the required element to the heteropoly acid. When the titrations were carried out with 10 ml of solution, a quarter of the cited amounts of phosphorus could still be determined successfully. The titration time was generally 7–15 min.

Titrations of other nitrogen-containing compounds

In addition to the nitrogen compounds cited above, similar titrations were carried out with brucine, acriflavine, antipyrine, ephedrine, oxine and hexamine. The results were as follows. Brucine behaved like strychnine acting with one nitrogen atom. Acriflavine acted at pH 1 and 7 with one nitrogen atom only. Ephedrine, even when used in double concentration (0.02 M), gave no precipitate at all. Antipyrine and oxine gave end-points which did not coincide with the calculated "end-points". Hexamine (0.02 M) either gave no precipitate or the readings were variable.

SUMMARY

Micro amounts of nitron, quinine, strychnine, papaverine, yohimbine, nicotine, atropine, morphine or phenanthroline were titrated heterometrically with silicotungstic, phosphotungstic or phosphomolybdic acids at pH 1 or 7. The heterometric curves and the compounds obtained were studied. The reverse titrations were also studied. Microheterometric determinations of large nitrogen-containing compounds and heteropoly acids are suggested.

RÉSUMÉ

Une méthode est décrite pour le microdosage de nitron, quinine, strychnine, papavérine, yohimbine, nicotine, atropine, morphine et phénanthroline, par titrage hétérométrique, au moyen d'hétéropolyacides (acide silicotungstique, acide phosphotungstique ou acide phosphomolybdique).

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Mikromengen von Nitron, Chinin, Strychnin, Papaverin, Yohimbin, Nikotin, Atropin, Morphin und Phenanthrolin durch heterometrische Titration mit Heteropolysäuren. Das Verfahren eignet sich auch im umgekehrten Sinne zur Bestimmung von Heteropolysäuren.

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Short Communications

The interference of thallium in the spectrophotometric determination of antimony as iodoantimonite

According to McCHESNEY[1], traces of antimony can be determined spectrophotometrically as iodoantimonite, SbI_4^-, by addition of potassium iodide and ascorbic acid to an antimony solution which is 3 N in sulphuric acid. Thallium interferes with this determination. As a rapid and simple method for the determination of traces of antimony in the presence of large amounts of thallium was required, an attempt was made to eliminate this interference.

A calibration graph was prepared following the procedure given below except that the antimony solutions were free from thallium and the centrifugation step was omitted. The equation of the graph was calculated by the method of least squares and is given in Table I. The procedure was then applied to solutions containing known

TABLE I

DATA FOR CALIBRATION GRAPHS

Thallium absent	*Thallium present*
$A' = 0.001541\,C$	$A' = 0.0225 + 0.001561\,C$
$s_b = 0.0000095$	$s_a = 0.0020$
$n = 16$	$s_b = 0.000016$
	$n = 36$

TABLE II

ABSORBANCE IN PRESENCE OF THALLIUM

Thallium µg/100 ml	*Absorbance measured*					
	50 µg of Sb/100 ml		*100 µg of Sb/100 ml*		*200 µg of Sb/100 ml*	
0	0.077		0.154		0.308	
25	0.077	0.078	0.154	0.155	0.308	0.305
50	0.082	0.079	0.155	0.153	0.306	0.310
75	0.086	0.082	0.159	0.161	0.315	0.308
100	0.106	0.106	0.185	0.177	0.340	0.334
200	0.098	0.094	0.186	0.182	0.331	0.336
300	0.098	0.105	0.178	0.181	0.339	0.334
400	0.098	0.098	0.176	0.172	0.331	0.337
500	0.097	0.103	0.179	0.182	0.332	0.329
1000	0.098	0.100	0.174	0.174	0.336	0.333

amounts of thallium and antimony. When less than 250 µg of thallium was present, no precipitate of thallous iodide was observed; the absorbances measured are shown in Table II. It can be seen that at each level of antimony, the absorbance increases with increasing amounts of thallium up to about 100 µg and then becomes almost

constant. The data given in Table II for the presence of 100–1000 μg of thallium were used to calculate the equation relating the measured absorbance, A', to the amount of antimony, C, by the method of least squares on the basis of a linear relationship, $A' = a + bC$. The standard errors of the intercept and the slope, s_a and s_b respectively, were also calculated. These results are also given in Table I.

The slopes of the two curves do not differ significantly on the 0.05-level, as shown by application of the t-test. It must, therefore, be assumed that the curves run parallel and that the amount of thallium has no influence on the slope of the curve when more than 100 μg is present. It can therefore be concluded that antimony can be determined in the presence of thallium by the procedure mentioned, provided that at least 100 μg of thallium is present and the curve with intercept, mentioned in Table II, is used. When less than 100 μg of thallium is present, the procedure can also be applied when an extra amount of thallium is added to the sample solution. It is then advantageous to add so much thallium that a reasonable precipitate is formed. The parallelism of the curves shows that no measurable amounts of iodoantimonite are removed from the solution with the thallous iodide precipitate. This is in contradiction with the findings of McCHESNEY[1].

The recommended procedure is as follows: To a solution containing 50 to 600 μg of antimony and at least 500 μg of thallium, add sufficient 36 N sulphuric acid that after dilution to 100 ml the solution is 3 N in acid.

Add 20 ml of potassium iodide–ascorbic acid solution (140 g of potassium iodide and 25 g of ascorbic acid dissolved in water and diluted to 250 ml) and make up to 100 ml. Leave the solution for at least 30 min and remove the precipitate by centrifugation. Measure the absorbance of the clear supernatant liquid at 425 mμ in a 4-cm cell against a blank. Prepare the blank in the same way but use water instead of the antimony–thallium solution and omit centrifugation.

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Note concernant le dosage potentiométrique du vanadium dans les aciers

Parmi les différents éléments entrant dans la composition des aciers, le vanadium est l'un de ceux difficiles à doser chimiquement, non seulement parce qu'il se trouve à des teneurs relativement faibles (<5%), mais parce qu'il accompagne souvent le tungstène dont la présence est gênante.

L'élimination préalable du tungstène par précipitation de l'anhydride tungstique[1] a été abandonnée depuis longtemps; l'entraînement du vanadium est inévitable et nécessite souvent le dosage colorimétrique du vanadium entraîné. Pour éviter ces longues manipulations qui diminuent la précision du dosage, on a été amené à engager le tungstène dans des complexes solubles très stables, non réductibles par le sulfate ferreux. Les complexes avec l'acide phosphorique[2-7] ou avec l'acide fluorhydrique[8] sont les plus employés à l'heure actuelle et se prêtent très bien aux différentes méthodes de titrage du vanadium.

La plupart des méthodes de titrage du vanadium décrites dans la littérature reposent soit sur la réduction du vanadate par le sulfate ferreux soit sur l'oxydation du sel de vanadyle par le permanganate de potassium.

(1) Titrage du vanadate par le sulfate ferreux

Après mise en solution et peroxydation de l'acier, certains auteurs[1,3,4,6,8-11] réduisent quantitativement le chromate et le vanadate formés par un excès de sulfate ferreux. Ils réoxydent alors sélectivement le sel de vanadyle, à froid, par un léger excès de permanganate et titrent le vanadate formé par une solution de sulfate ferreux. Les variantes de cette méthode résident principalement dans le mode de destruction du permanganate en excès: WILLARD ET YOUNG[8], DUCRET[10] SILVESTRE ET HURTH[3] et ARRIBAS JIMENO[4] utilisent l'azoture de sodium; LANG ET KURTZ[1], BÜNGER[6] et SHAW[11] ajoutent un léger excès de nitrite dont ils détruisent l'excès par l'urée[1,6] ou l'acide sulfamique[11] tandis que DICKENS ET THANHEISER[9] emploient l'acide oxalique.

Cette méthode, la plus employée à l'heure actuelle, présente néanmoins quelques inconvénients: la destruction du permanganate est délicate et exige un réducteur ne réagissant pas avec le vanadate formé; de plus, la réduction du vanadate formé par le sulfate ferreux ne serait pas toujours quantitative, à froid, et en présence de tungstène[2].

(2) Titrage du sel de vanadyle par le permanganate

L'oxydation du sel de vanadyle en vanadate par le permanganate constitue la base de plusieurs méthodes de titrage du vanadium[2,5,12,13]. Après réduction de la solution d'attaque par un excès de sulfate ferreux, on réoxyde d'abord quantitativement le sel ferreux par le bichromate[12] ou le persulfate ammonique[5] puis

on titre le sel de vanadyle par le permanganate. Cette méthode n'est évidemment valable que si le réactif employé pour l'oxydation du sulfate ferreux est sans action sur le sel de vanadyle.

Pour éviter l'oxydation sélective de l'excès de sel ferreux, CLAASSEN ET CORBEY[2] titrent le sel ferreux en excès et le sel de vanadyle par le permanganate en suivant l'évolution de la réaction par potentiométrie.

En suivant le mode opératoire préconisé par ces auteurs, nous obtenons fréquemment des résultats par excès comme l'indiquent les chiffres ci-après:

Acier B.C.S.241 (V = 1.54%); trouvé : 1.63, 1.65 et 1.61%
Acier B.C.S.220 (V = 1.35%); trouvé : 1.48%.
Acier B.C.S.256 (V = 0.360%); trouvé : 0.40%.

L'emploi de concentrations plus fortes en acide sulfurique et en acide phosphorique et la substitution de l'acide nitrique au permanganate pour la peroxydation n'ont pas amélioré les résultats.

Quoique l'oxydation du chrome soit possible en présence de permanganate, nous ne pouvons attribuer les écarts observés à cette réaction. En effet, nous n'avons trouvé aucune erreur importante dans le titrage de solutions synthétiques dont la composition était voisine de celles obtenues pour les aciers analysés. A cet effet, nous avons choisi un acier contenant 0.21% Si, 13.25% Mn, 0.07% Ni et 0.23% Cr et nous avons ajouté à la solution d'attaque des quantités connues de vanadium, de molybdène et de tungstène. Comme le montrent les chiffres ci-dessous, le dosage du vanadium reste exact.

0.5 g d'acier + 0.0133 g de vanadium; trouvé : 0.01325 g V.

0.5 g d'acier + 0.0133 g de vanadium + 0.025 g de chrome; trouvé : 0.01338 g V.

0.5 g d'acier + 0.0133 g de vanadium + 0.025 g de chrome + 0.01 g de molybdène + 0.05 g de tungstène; trouvé : 0.01315 g V.

L'oxydation des carbures, du carbone et du tungstène par le permanganate étant souvent longue et difficile, nous avons préféré attaquer l'acier par un mélange d'acide nitrique, chlorhydrique et phosphorique puis peroxyder par l'acide perchlorique à l'ébullition. Cette mise en solution, préconisée par WILLARD ET GIBSON[14] et reprise par SILVESTRE ET HURTH[3], assure une oxydation complète et nous a donné cette fois des résultats corrects pour le vanadium par la methode potentiométrique de CLAASSEN ET CORBEY[2]. Ceci semble prouver que les résultats trouvés par excès seraient dus à la présence de carbures non oxydés lors de l'attaque utilisant la peroxydation par le permanganate.

Mode opératoire

Attaquer l'acier par un mélange d'acide chlorhydrique, nitrique et phosphorique concentrés dont la quantité dépend de la prise d'essai: 15 ml de HCl 12 *N* + 5 ml de HNO_3 14 *N* + 10 ml de H_3PO_4 (d=1.69) pour une prise de 1 g d'acier (teneur en vanadium supérieure à 1%) et par 20 ml de HCl 12 *N*, 7 ml de HNO_3 14 *N* et 20 ml de H_3PO_4 (d = 1.69) pour une prise de 3 g (teneur en vanadium inférieure à 1%). Porter au bain-marie pour faciliter l'attaque et, lorsque le dégagement d'hydrogène cesse, ajouter suivant la prise d'essai, 20 ou 30 ml d'acide perchlorique à 70%. Evaporer jusqu'à fumées blanches perchloriques et compléter l'oxydation en faisant

bouillir la solution quelques minutes. Après refroidissement complet, reprendre par 40 ml d'eau, ajouter du sulfate ferreux solide jusqu'à réduction complète du bichromate et du vanadate et, en présence de tungstène, faire bouillir la solution pour réduire complètement le vanadate[2]. Amener le potentiel entre 400 et 420 mV *vs.* S.C.E. à l'aide de permanganate concentré puis titrer avec du permanganate 0.05 *N* à 0.02 *N*. Après le premier saut de potentiel qui se situe aux environs de 550 mV *vs.* S.C.E., diluer la solution à 400 ml et l'amener à 50° avant de poursuivre le titrage.

La réaction d'oxydation du sel de vanadyle, presque instantanée au début du titrage, devient plus lente au voisinage du terme. Le saut de potentiel est net (environ 200 mV); il débute vers 700 mV *vs.* S.C.E. et permet la détermination précise du point équivalent.

Résultats

L'application de cette méthode à plusieurs aciers standards nous a donné les résultats suivants.

Aciers[a]	% *V renseigné*	*Limite des % V renseignés*	% *V trouvé*
B.C.S.241/1	1.57	1.54/1.59	1.58,1.59,1.56
B.C.S.241	1.54	1.51/1.58	1.56,1.56
B.C.S.256	0.360	0.348/0.371	0.355,0.354
B.C.S.220	1.35	1.32/1.38	1.39,1.40,1.385
B.C.S.258	0.645	0.617/0.660	0.647,0.653
B.C.S.224	0.24	0.231/0.250	0.252,0.258
B.C.S.254	0.52	0.501/0.540	0.524,0.523
B.C.S.252	0.460	0.446/0.475	0.460,0.461
B.C.S.225	0.265	0.255/0.275	0.264,0.265

[a] Composition du pourcentage:

B.C.S.241/1 (W,19.61; Cr, 5.03; V, 1.57; Mo, 0.51; Co, 5.64; C, 0.85; Si, 0.33; S, 0.033; P, 0.021; Mn, 0.295; Ni, 0.075; Cu, 0.10; Sn, 0.025).
B.C.S.241 (W, 20.28; Cr, 5.12; V, 1.54; Mo, 0.54; Co, 5.84; C, 0.83; Si, 0.22; S, 0.035; P, 0.025; Mn, 0.23; Ni, 0.19; Cu, 0.15; Sn, 0.035).
B.C.S.256 (Si, 0.13; Mn, 1.21; Ni, 0.185; Cr, 2.34; Mo, 0.535; V, 0.360; Cu, 0.23).
B.C.S.220 (W, 6.74; Mo, 4.17; Cr, 4.61; V, 1.35; Co, 0.67; C, 0.86; Si, 0.30; S, 0.039; P, 0.024 Mn, 0.25; Ni, 0.15; Cu, 0.14; Sn, 0.04; As, 0.032).
B.C.S.258 (Si, 0.81; Mn, 0.79; Ni, 0.048; Cr, 3.07; Mo, 0.425; V, 0.645; Cu, 0.185; Co, 0.029; Sn 0.009).
B.C.S.224 (Cr, 1.46; V, 0.24; C, 0.390; Si, 0.30; S, 0.029; P, 0.012; Mn, 0.695; Ni, 0.10; Mo, 0.02; Cu, 0.07; As, 0.03; Co, 0.01; Sn, 0.01).
B.C.S.254 (Si, 0.295; Mn, 0.525; Ni, 2.08; Cr, 0.535; Mo, 1.29; V, 0.52; Cu, 0.11; Co, 0.029; Sn, 0.005).
B.C.S.252 (Si, 0.245; Mn, 0.016; Ni, 4.10; Cr, 0.20; Mo, 0.007; V, 0.460; Cu, 0.11; Co, 0.04; Sn, 0.004).
B.C.S.255 (Si, 0.625; Mn, 1.11; Ni, 0.565; Cr, 0.96; Mo, 1.41; V, 0.265; Cu, 0.24; Sn, 0.007; Co, 0.006; Al, 0.057).

La comparaison des résultats obtenus avec les résultats renseignés dans les bulletins d'analyse des aciers standards montrent que la méthode est exacte, aux erreurs de mesures près, et que le tungstène, le molybdène, le chrome, le nickel, le cobalt, le cuivre, le manganèse, le silicium, l'étain et l'aluminium ne gênent pas le titrage potentiométrique du vanadium.

Précision de la méthode

Les dosages effectués sur 10 attaques différentes d'un même acier ont donné les résultats suivants:

Acier au tungstène fortement allié (A) % *V*		*Acier sans tungstène peu allié (B)* % *V*	
	1.921		0.261
	1.924		0.263
	1.935		0.267
	1.935		0.265
	1.923		0.265
	1.940		0.261
	1.912		0.277
	1.940		0.262
	1.928		0.261
	1.911		0.262
Moyenne:	1.927	Moyenne:	0.264

L'écart type $\sqrt{\Sigma e^2/(n-1)}$ déterminé à partir des mesures précédentes est de 1.5% pour l'acier *A* et de 2% pour l'acier *B*.

Nous tenons à remercier Monsieur le Professeur G. DUYCKAERTS et Monsieur G. MICHEL, Chef de Travaux, pour les échanges de vue fructueux que nous avons eus ensemble et pour les conseils judicieux qu'ils nous ont prodigués au cours de ce travail.

G. ROLAND

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Book Reviews

Atlas of Analysis Lines, by HALINA JAFFE, Hilger and Watts Ltd., London, 1962, 57 cards, £ 26.5.0.

This atlas of selected spectral lines of 69 elements is printed on 31 × 16 cm cards in a stiff plastic-covered folder. Seven printed cards carry instructions for the use of the atlas, together with tables of analysis lines, arranged by element and by wavelength, which include limits of detection for each line using a direct current graphite arc. The atlas consists of 50 glazed cards presenting a series of three exposures of an iron arc spectrum taken on a Hilger E478 quartz-glass spectrograph, using quartz optics for the ranges 2478–3500Å and 3324–9000Å and glass for the range 3981–5500Å. Each card carries a 30 × 2.4 cm reproduction of a section of the iron spectrum. The selected analysis lines of the other elements are shown diagrammatically, above and below the iron spectrum, as uniform 2.4 cm long black lines on a white base, the element and wavelength being identified at the bottom only. It would have been more convenient if this information had also been printed, reversed, at the top, as not all workers examine their plates with the short wavelength end to the left: such standard atlases as those of Gatterer and Hilger R.U. powder put the long wavelength to the left. It might also have been useful if the wavelength range covered by each card had been clearly indicated in one corner, and if the wavelengths of the iron lines had been given.

Although of quite general utility to all users of prism spectrographs, the atlas is primarily intended for use with a Hilger H89 or similar spectrum projector, the image of the plate being projected at the appropriate magnification on to the card and coincidence obtained by matching the iron lines. Some sections of the iron arc spectrum on which the atlas is based are not as sharply focussed as is possible with an H478 spectrograph in good adjustment, but the definition is acceptable for most purposes. The atlas should prove valuable to the inexperienced worker, provided that he appreciates the possibility of line coincidence. It should facilitate, if not eliminate, the lengthy process of preparing marked plates during the initiation of spectrographic work, and also prove a useful tool for the experienced worker. The selection of marked lines, varying from one to eleven per element, is of necessity arbitrary. More lines could readily have been included, as some of the cards are relatively empty and many more lines are given in the somewhat similar but much less well-produced atlases of Brode or Kalinin *et al.* The lines chosen are probably adequate for element identification purposes, but may not always be sufficient to cover the requirements of quantitative measurement. For instance, only the two strong copper lines are quoted. Once an appropriate additional line has been found, its position could no doubt readily be marked on the atlas for future use.

The complete atlas is expensive, but the three ranges can be obtained separately at £ 10.10.0 each. It serves a useful purpose, and despite its shortcomings should be available in any well-equipped spectrographic laboratory.

R. L. MITCHELL (Aberdeen)

Mises au point de Chimie analytique pure et appliquée et d'analyse bromatologique publiées sous la direction de J. A. GAUTIER, Neuvième Série, Masson et Cie, Paris, 1961, 210 pages avec 47 figures et 31 Tableaux, 40 N.F.

Comme les précédentes, cette 9ème Série comporte des études très variées. Rappelons qu'elles comportent l'exposé d'un sujet rendu accessible aux non-spécialistes, puis la description des développements récents, y compris souvent des travaux originaux de l'auteur.

Les sujets traités ici sont:

Utilisation de la Chromatographie en phase gazeuse dans l'analyse des médicaments par L. DOMANGE et MLLE S. LONGUEVALLE.

Les possibilités de la spectrophotométrie infrarouge en analyse fonctionnelle par J. GUY.

Tendances actuelles de la microanalyse organique par R. LÉVY.

Nouveaux développements dans l'emploi de l'oxydation periodique par P. MALANGEAU.

Méthodes de dégradation de l'hétérocycle indolique et leurs applications à l'analyse structurale par C. MENTZER.

La spectrographie Raman et infra-rouge dans l'étude des fonctions acétylénique, allénique, éthylénique conjugué par M. MIOCQUE.

Le problème du traitement des aliments par les radiations ionisantes par P. NAVELLIER.

Progrès récents dans le contrôle des médicaments végétaux par chromatographie et électrophorèse sur papier par R. PARIS.

Cet ouvrage, précieux du pharmacien, sera aussi très utile à de nombreux chimistes.

C. CHARLOT (Paris)

Treatise on Analytical chemistry, édité par I. M. KOLTHOFF et P. J. ELVING avec la collaboration de E. B. SANDELL, Partie II, *Chimie analytique des éléments*, Volume 7, Interscience Publishers, New York, (1961), xxiii + 567 p., 139 s.

Ce volume comprend le soufre, le selenium, le tellure, le fluor, le chlore, l'iode, le manganèse et le rhénium. Chaque partie est présentée par un ou plusieurs spécialistes particulièrement compétents, ce qui entraîne parfois un manque d'homogénéité; par contre, le choix judicieux des méthodes proposées, l'ample documentation qui s'y trouve, non seulement dans le domaine de l'analyse, mais aussi dans celui de la chimie minérale, en fait un ouvrage de valeur et qui rendra d'inappréciables services. A titre d'exemple, citons les principaux chapitres concernant le fluor:

I. Introduction: occurrence–Procédés industriels pour la production du fluor, de l'acide fluorhydrique, des fluorures et des composés fluorés organiques–Toxicologie et moyen de protection, premiers soins. II. Propriétés du fluor et de ses composés: propriétés physiques, électrochimiques, optiques, chimiques. III. Echantillonnage. IV. Séparation du fluor: traitement préliminaire, fusion, évaporation–décomposition des composés fluorés organiques, – séparation du fluor par distillation et autres métho-

des telles que échangeurs d'ions, extractions, adsorption, etc. V. Détection et identification des fluorures inorganiques et organiques – Tests physiques. VI. Détermination du fluor et des fluorures – gravimétrie, titrimétrie, photométrie, méthodes physiques: polarographie, ampérométrie, analyse radiochimique. VII. Analyse du fluor et de ses composés. VIII. Détermination et analyse des composés du fluor: spectrophotométrie moléculaire, spectrométrie de masse, résonance magnétique nucléaire – Diffraction des rayons X, indice de réfraction, vitesse du son, conductibilité thermique, moment dipôle, constante diélectrique. XI. Détermination du fluor dans les substances biologiques, les engrais, les phosphates, le sol, les aliments, les roches, les minéraux, les eaux, l'air et les gaz, etc. X. Procédés recommandés . . . Comme on le voit, une documentation considérable, bien ordonnée, de nombreux tableaux de constantes (potentiel ox–red, constante acide–base constante de complexes, propriétés physiques et chimiques . . .), souvent présentés de façon originale.

Il y a peu de considérations théoriques, mais on trouve des précisions concernant la sensibilité, les erreurs, de même que les possibilités et les limites des méthodes présentées et des suggestions quant à leur choix. Un bel ouvrage.

D. MONNIER (Genève)

Anal. Chim. Acta, 28 (1963) 98–99

Physical Methods in Chemical Analysis, Volume IV. Ed. WALTER G. BERL, Academic Press, New York and London, pp. xi + 476, $16.00 or 114 s. 6d.

This most recent addition to the well-known series *Physical Methods in Chemical Analysis* deals exclusively with methods of separation. As with the previous volumes, the individual sections have been contributed by several authors, each recognized in the particular subject chosen for review.

The eight separate sections cover methods of separation which fall into four distinct categories: those depending on transport phenomena (dialysis and thermal diffusion), on electrical or magnetic properties, on phase equilibria (ion exchange, adsorption, solvent extraction), and on the use of inclusion compounds and molecular sieves.

The importance of separation methods to the analytical chemist need hardly be stressed here. Although some of the methods and techniques described in this volume may be less well-known or used by analytical chemists, it is always useful to have at hand a clear and concise account of such methods should the need for their use arise. The growth of separation by solvent extraction in recent years is well indicated by the size of the chapter dealing with this subject; it covers 140 pages and is extremely well presented. It may be invidious to single out one chapter for special mention, but the wealth of information so admirably documented must appeal to all analytical chemists interested in solvent extraction methods in inorganic analysis.

The aim of the individual sections is to provide comprehensive reviews of the various techniques, both from the theoretical and practical aspects. In this way, information not readily available to very many chemists is presented in its most acceptable form. This volume maintains the standards set up by its predecessors and is a welcome addition to this extremely useful and informative series.

W. I. STEPHEN (Birmingham)

Anal. Chim. Acta, 28 (1963) 99

Physical Aids to the Organic Chemist, by M. St. C. FLETT, Elsevier, Amsterdam, 1962, xii + 388 pp., 45s.

There are many excellent volumes discussing physical theories in organic chemistry and a number of advanced monographs (*e.g.* Weissberger) describing physical techniques in organic chemistry. Mr. Flett has written an excellent introductory text in the latter category which is certain to achieve a well-deserved popularity.

He has chosen to describe a selection of instrumental techniques which have been systematically employed in the industrial research laboratory with which he is associated (I.C.I. Dyestuffs Division). These are covered as follows: adsorption, partition and gas-liquid chromatography, pp. 6–58; zone refining, pp. 59–72; electronic absorption spectra, pp. 73–137; infra-red methods, pp. 138–223; e.s.r. spectra, pp. 224–254; n.m.r. spectra, pp. 255–308; mass spectrometry, pp. 309–351; X-ray studies, pp. 352–379.

These sections include a brief account of the essential principles, an outline of experimental apparatus and procedures and numerous illustrative examples, providing an admirable introduction to the scope of the methods. To take one topic only: the electronic (*i.e.* uv and visible) absorption spectra are illustrated with examples of qualitative and quantitative analyses, diagnostic uses, studies of equilibria and reaction rates and even flash photolytic processes. A remarkable amount of clear and well coordinated information is presented very succinctly. The volume is based on extensive practical experience. Only in the final chapter (X-ray crystallography) does the over-brief presentation fail to achieve an adequate appreciation of the essentials. It was disappointing too, that micro-wave rotational spectra received no treatment.

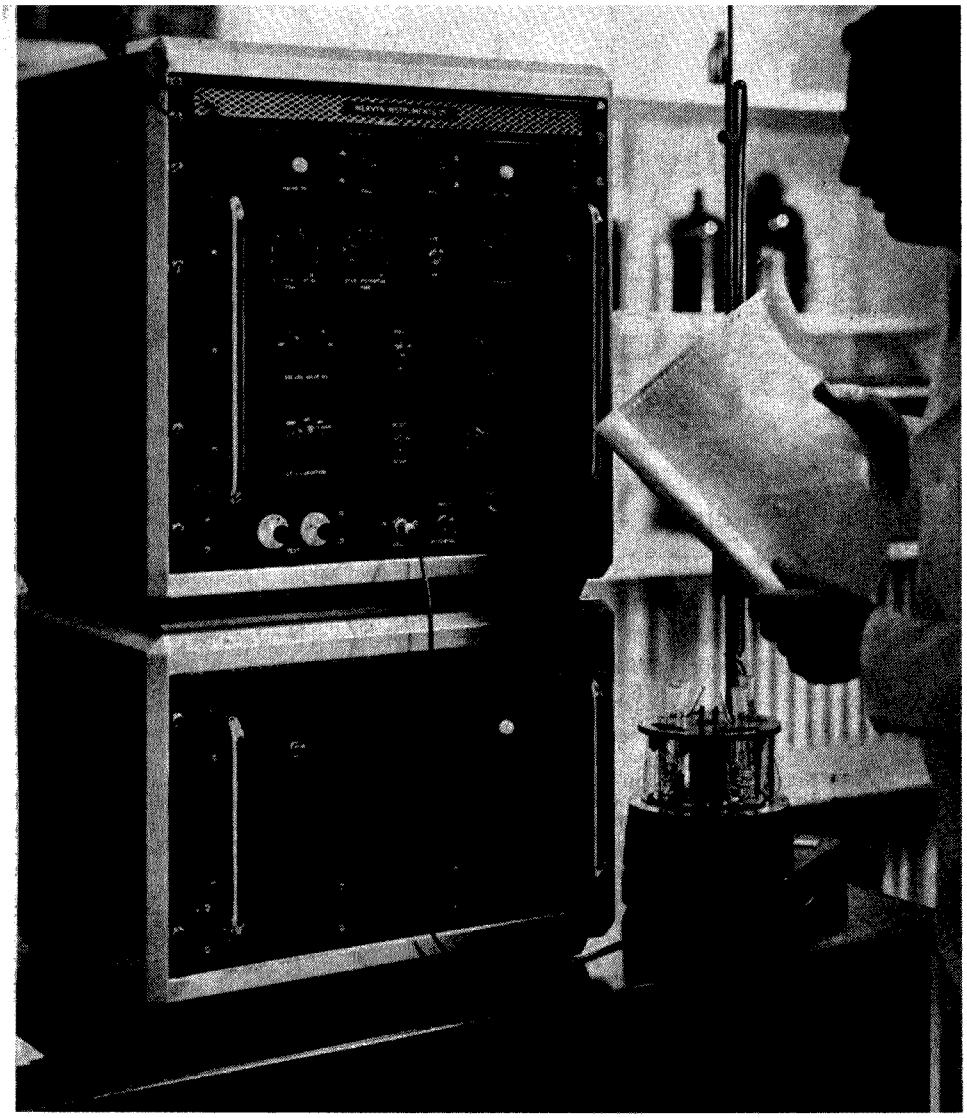
With those topics he has discussed, the author has produced accounts of exceptional value for teachers and students of modern physico-chemical methods. The modest price will add to the success of this volume.

MANSEL DAVIES (Aberystwyth)

Methods of Biochemical Analysis, Volume 10, edited by DAVID GLICK, Interscience–Wiley, New York, 1962, ix + 399 pp., 109 s.

The aim of this series of volumes in providing authoritative reviews on methodology and instrumentation in the field of biochemistry and peripheral subjects has certainly been maintained by this latest addition to the series. The international character of the volume is reflected by the fact that there are contributions from five countries. A good balance has been maintained between specific and general methods with gas-liquid chromatography of carbohydrates, dialysis, counter current distribution and fractionation of cell particles included in the latter group. A more specific treatment is given to protein thiol groups, sodium and potassium determination, UDP and two-substrate enzyme systems, the determination of flavins and the microscopic determination of cholesterol. A glance at the cumulative index for this series of volumes reveals the wide range of subjects covered and clearly emphasises their value to the practising biochemist and in many cases to the chemist.

A. B. FOSTER (Birmingham)



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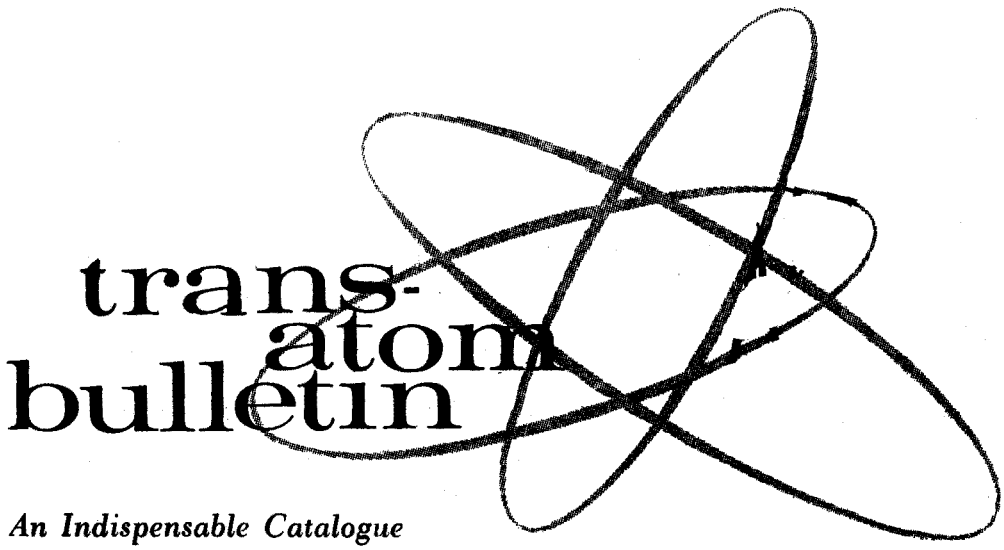

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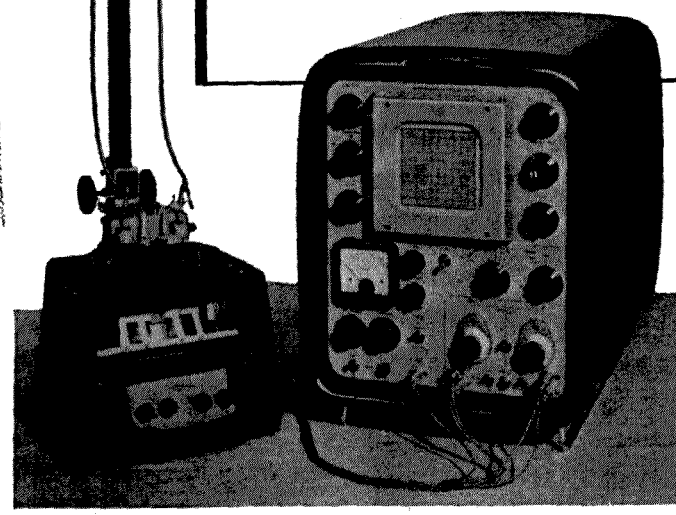

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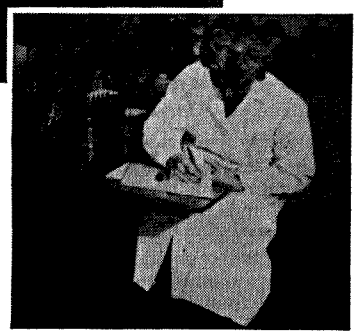

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A reagent for the spectrophotometric determination of **Ta** in the presence of **Zr, Nb** or **Ti.** (see V. A. Nazarenko and M. B. Shustova, *Zavodskaya Lab.* **2B,** 1283 (1957); C.A. **53,** 13874c (1959)). CODE 3862·3. Price 1g 9/9, 5g 40/-.

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