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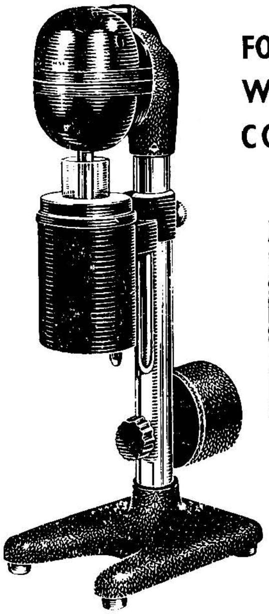

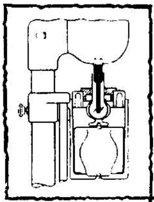

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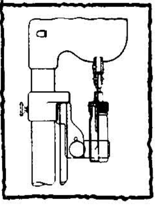

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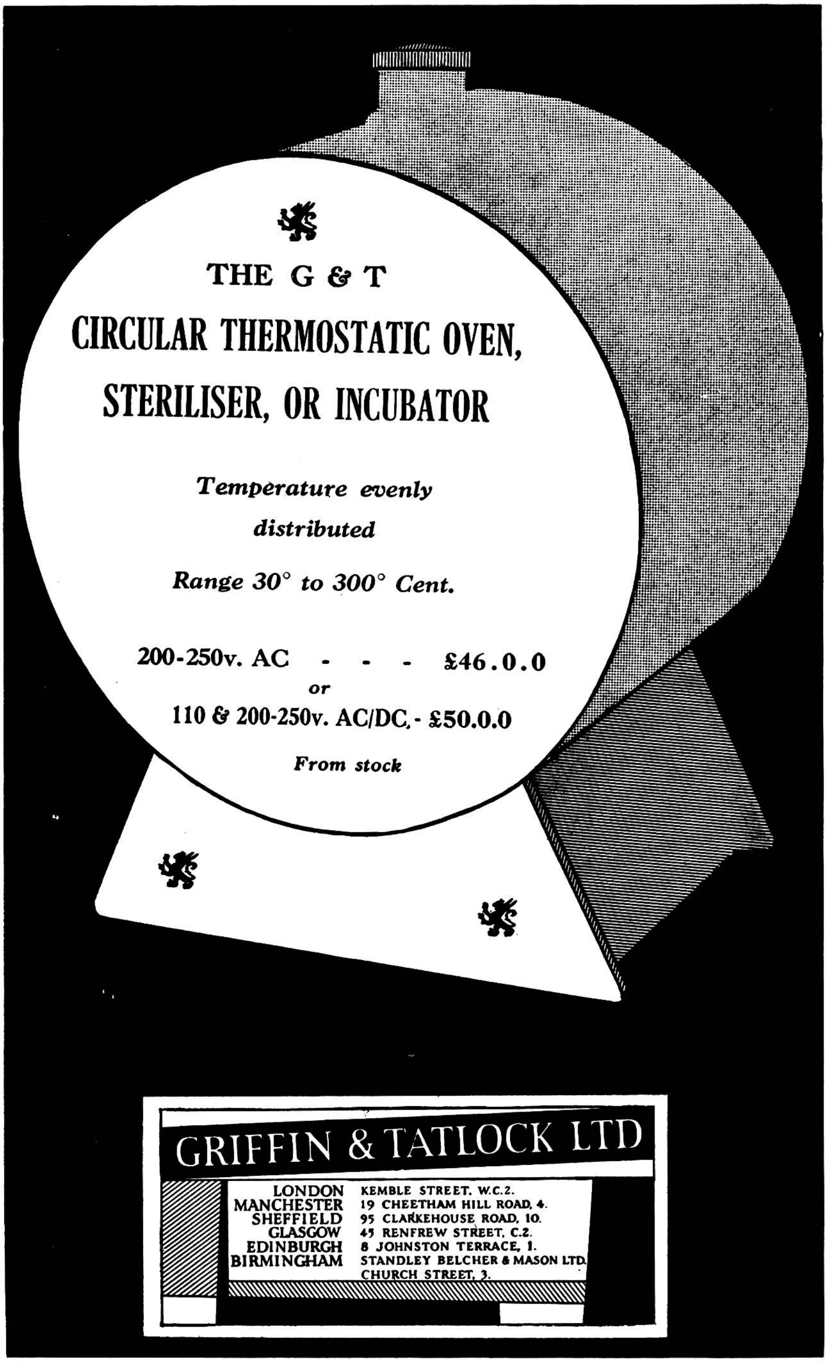

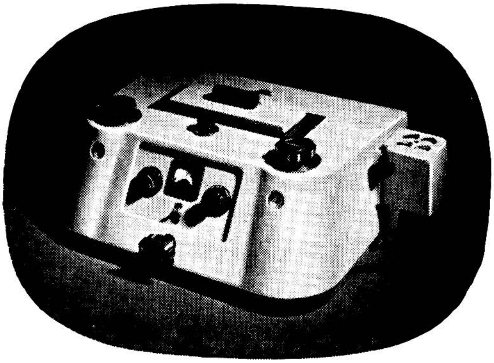

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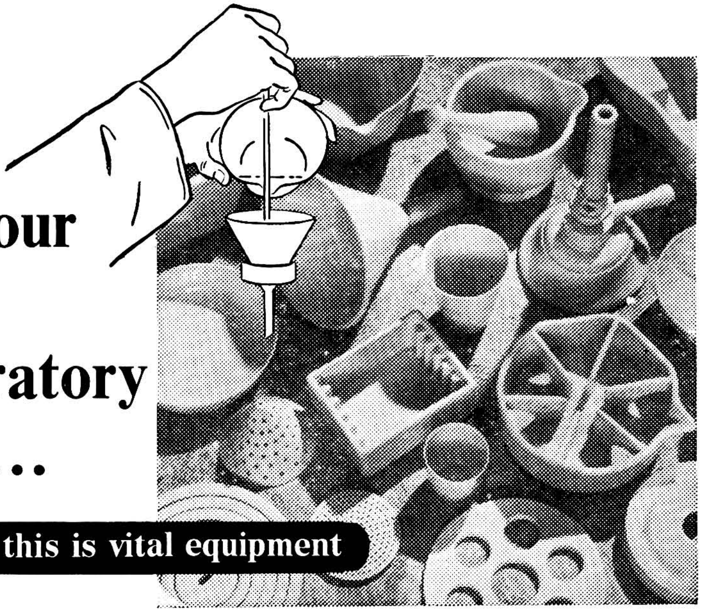
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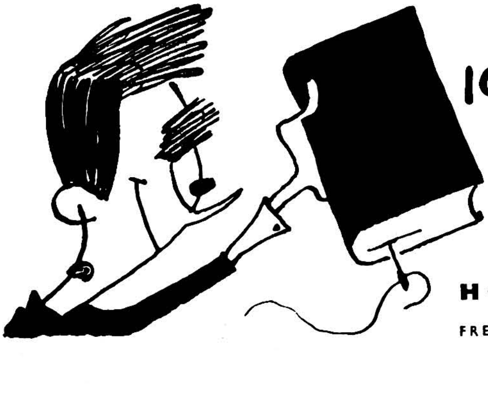

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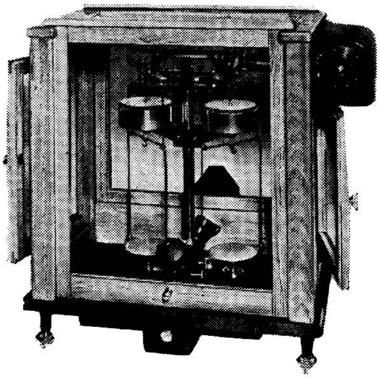

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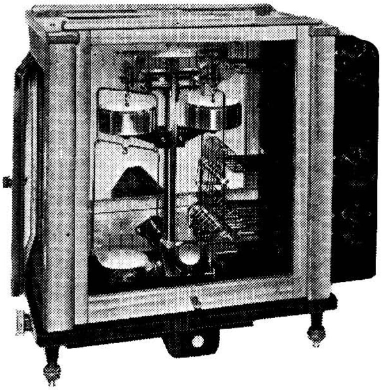

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THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

ORDINARY MEETING

An Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, May 5th, 1954, in the meeting room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. D. W. Kent-Jones, F.R.I.C.

The following papers were presented and discussed: "The Determination of Phosphate in the Presence of Soluble Silicates: Application to Basic Slag," by H. N. Wilson, F.R.I.C. (presented by A. E. Heron, F.R.I.C.); "The Spectrophotometric Estimation of Total Penicillins by Conversion to Penicillenic Acid and the Importance of Copper in Controlling the Reaction," by F. G. Stock, M.Pharm., Ph.C., A.R.I.C.; "Micro Method for the Determination of Bromide in Presence of Chloride," by G. Hunter, M.A., D.Sc., and A. A. Goldspink.

NEW MEMBERS

Ordinary Members

Syed Zafar Ahmad, M.Sc. (Osmania Univ.); Alan Bertram Bentley, B.Sc. (Birm.), A.R.I.C., A.C.T. (Birm.); Herbert William Bryan Collier, A.R.I.C.; W. Donald Cooke, B.S. (St. Joseph's), M.S., Ph.D. (Pennsylvania); Promod Kumar Das, B.Sc. (Calcutta), A.I.C. (India); James Caithness Eaton, B.Sc., M.B., Ch.B. (Glas.), F.R.I.C.; Mahdi Khoja, B.Sc. (Liv.); Alfred George Knight, B.Sc. (Lond.); Colin John Owen Rhonabwy Morris, Ph.D. (Lond.), M.Sc. (Wales), F.R.I.C.; Edward Stanley Fairfield Rogans, F.R.I.C.; Alan Donald Wilson, B.Sc. (Lond.); Lionel George Young.

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INAUGURAL MEETING OF THE WESTERN SECTION

The Inaugural Meeting of the Western Section was held at 12 noon on Saturday, May 8th, 1954, at the Technical College, Newport, Monmouth. The President of the Society, Dr. D. W. Kent-Jones, was in the Chair, and was supported by the following members of the Council: Mr. T. McLachlan, Vice-President; Dr. K. A. Williams, Honorary Secretary; Mr. N. L. Allport, Honorary Assistant Secretary; Mr. T. W. Lovett, Chairman of the North of England Section; Dr. A. M. Ward, Chairman of the Microchemistry Group; Miss M. Corner and Dr. D. C. Garratt.

The following Officers and Members of Committee were elected:—*Chairman*—Mr. H. J. Evans. *Vice-Chairman*—Mr. P. J. C. Haywood. *Hon. Secretary*—Dr. G. V. James. *Members of Committee*—Messrs. S. Dixon, A. J. Dobbins and J. S. Hughes.

The Rules of the Section were then adopted. At the end of the business session Mr. H. J. Evans took over the Chair from the President.

The afternoon session was occupied with a paper presented by Dr. D. W. Kent-Jones on "Alcohol Determination and its Medico-Legal Aspects"; a discussion followed.

PHYSICAL METHODS GROUP

The Forty-fifth Ordinary Meeting of the Group was held at 6.30 p.m. on Tuesday, April 6th, 1954, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. Mr. A. A. Smales, B.Sc., F.R.I.C., was in the Chair.

The following papers on "Mass Spectrometry" were presented and discussed: "The Mass Spectrometer as an Analytical Tool," by G. P. Barnard, B.Sc., Ph.D., F.Inst.P., A.M.I.E.E.;

"Some Applications of the Mass Spectrometer to Studies of Chemical Reaction," by R. I. Reed, Ph.D., A.R.I.C. (see summary below); "Quantitative Analysis of Mixtures of Organic Compounds by Mass Spectrometry," by Dr. F. Hageman.

SOME APPLICATIONS OF THE MASS SPECTROMETER TO STUDIES OF CHEMICAL REACTION

DR. R. I. REED said that the mass spectrometer had many applications to chemical problems, and without its use much information would be unobtainable, or at best deduced by inference by other means. He described three such uses of mass spectrography in studies of chemical reactions.

(*i*) The identification and estimation of small quantities of material, although limited to compounds of a suitable volatility, was of considerable assistance in the particular problem of the examination of by-products from chemical reactions. The recognition of these might otherwise require the use of large-scale experiments, which was not always desirable, nor, with isotopic "tracer" experiments, practicable.

(*ii*) The determination of the abundance of stable "tracer" elements in reaction systems, where the use of stable isotopes was convenient (carbon-13), or essential, as with nitrogen, which was used in studies of metabolic processes as well as investigations into reaction mechanisms.

(*iii*) Mass spectrometry might also be used as a substitute for alternative methods of isotopic analysis where, while not so convenient as the customary methods, its application became essential by reason of the small quantities available for examination. In particular, such studies included the determination of the deuterium content of a limited class of aromatic organic acids by assay of not more than 2-mg samples. Attempts to minimise some of the difficulties inherent in this method were described.

COMMITTEES, 1954–1955

THE Council of the Society has appointed the following Committees—

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OTHER COMMITTEES—

In view of the formation of the Association of Public Analysts, the Council considers that the Public Analysts and Official Agricultural Analysts Committee is no longer necessary and has not re-appointed it.

The constitution of the Analytical Methods Committee is being reviewed by the Council and its Policy Committee, and an announcement about it will be made later.

The Absorptiometric Determination of Niobium in Some African Low-grade Minerals and Mineral-dressing Products

By G. W. C. MILNER and A. A. SMALES

(Presented at the meeting of the Society on Wednesday, November 4th, 1953)

A method is described for the determination of 0·05 per cent. to at least 16 per cent. of niobium pentoxide in head samples and mineral-dressing fractions produced during treatment of Sukulu soils (mainly magnetite, apatite and quartz) and Nigerian granite (mainly quartz and cryolite). After chemical attack on the sample, the niobium is separated from the bulk of the other materials by precipitation with tannic acid and cinchonine with silica as carrier, and is finally determined absorptiometrically with potassium thiocyanate. The separation steps need not be quantitative because radiometric correction for losses is made by incorporating niobium-95 tracer in the procedure.

The need arose for a knowledge of the niobium content of certain phosphatic and siliceous ores and of the fractions produced during mineral-dressing operations designed to concentrate the niobium. The former ore originated from Sukulu, Uganda, and consisted mainly of magnetite (Fe_3O_4), apatite ($3Ca_3P_2O_8.CaF_2$) and quartz, together with small amounts of zircon ($ZrSiO_4$), baddeleyite (ZrO_2), ilmenite ($FeTiO_3$) and pyrochlore (the niobium-bearing mineral). The siliceous ore originated in Nigeria (Nigerian granite) and contained riebeckite (ferrous sodium silicate), cryolite and pyrochlore in addition to the main constituent, quartz.

Burstall and Williams have recently published a method[1] for the determination of niobium in this type of mineral; it involves a preliminary concentration of niobium and tantalum from a 10-g sample by acid hydrolysis with sulphur dioxide and then a separation of the two elements from each other chromatographically in fluoride solution with ethyl methyl ketone as solvent. After evaporation of the large volumes of solvent used, the niobium and tantalum are determined gravimetrically. This method has some disadvantages, particularly from the point of view of speed. The problem was therefore approached by attempting to find in the first instance a sensitive physico-chemical technique for the determination of microgram amounts of niobium. If this were possible, a very much smaller quantity of sample would be necessary, which would reduce the time required for dissolving the ore and also for the separations involved. It might also be possible to avoid complete separation of niobium from all other elements present.

POSSIBLE METHODS FOR THE DETERMINATION OF MICROGRAM QUANTITIES OF NIOBIUM—

The possibility of applying emission spectroscopy to the determination of microgram quantities of niobium was obvious and work on this approach was initiated and is reported separately by Thorne.[2]

Polarography did not appear promising, as Stromberg and Reinus[3] failed to detect reduction steps for niobium^{V} in the following base electrolytes: sulphuric acid, tartaric acid, hydrochloric acid, salicylic acid and ammonium oxalate. From nitric acid solutions these workers observed a wave at —0·8 volt against the saturated calomel electrode, which they attributed to a hydrogen reduction step catalysed by niobium^{V}, but such waves are not attractive for the present purpose. The reduction step for niobium from a base solution consisting of 10 *N* hydrochloric acid and 20 per cent. v/v of ethylene glycol, recently reported by Vivarelli and Cozzi,[4] may be applicable to this problem.

Radioactivation cannot be recommended for this purpose. Apart from the requirement of an irradiation source, the half-life of niobium-94, produced by neutron irradiation of natural niobium, is only 6·6 minutes, which is too short for the radiochemical separations that would be necessary.

Absorptiometric techniques, however, appeared more promising, and according to Sandell,[5] a number of reagents produce stable colours with niobium, although the majority are not very sensitive for the element, nor does any one appear to be specific. The colour reactions with hydrogen peroxide or with quinalizarin occur satisfactorily only in concentrated sulphuric acid solution, which is troublesome to handle. Pyrogallol and thiocyanate have been used with success by Russian workers, but the former seems to be rather less sensitive. The latter reagent was therefore used in this investigation. It has been stated[6] that niobium should be in the tervalent state to give a yellow - orange coloured product with thiocyanate ions in hydrochloric acid solutions, but in fact recent work by Milner[7] and by Lauw-Zecha, Lord and Hume[8] has shown that reduction of the niobium is unnecessary. However, although the omission of a reducing agent improved selectivity in that interference by tungsten and molybdenum was reduced, iron then became a major interference. More recently, Freund and Levitt[9] and Lauw-Zecha *et al.* have studied the niobium - thiocyanate coloured complex in detail. The former workers used a water - acetone homogeneous medium for the development of the coloured complex, but Lauw-Zecha preferred to extract the complex into ether. From the point of view of speed, the homogeneous medium is to be preferred, and Freund and Levitt's conditions have therefore been used in this work, optical densities being measured with a Uvispek spectrophotometer or the Spekker absorptiometer with Chance OV1 and Wratten No. 2 filters. The errors produced by other elements are shown in Table I in a slightly different form from those reported by Freund and Levitt. Fortunately tantalum is not important in the types of mineral under discussion, because the niobium occurs as pyrochlore in which the tantalum to niobium ratio is less than 1 to 10. This ratio is unlikely to be altered by any of the mineral-dressing treatments proposed. Most of the other elements listed as interfering do not occur in the original ores at a sufficiently high level to cause difficulty in the niobium determination and there is the possibility of avoiding separations altogether. However, in the mineral-dressing operations, niobium must be determined in the pyrochlore-deficient materials, and the ratio of the interfering element to niobium is then likely to be increased. For this reason we have attempted to develop a simple procedure for separating the microgram quantities of niobium that occur in a 200-mg sample from the major constituents of that sample.

TABLE I

THE PERCENTAGE ERROR IN THE DETERMINATION OF 125 μg OF NIOBIUM PENTOXIDE CAUSED BY INTERFERING ELEMENTS

Nature of interfering element	Error when the ratio of interfering element to Nb_2O_5 is—		
	10 to 1, %	1 to 1, %	1 to 10, %
Ta_2O_5	+11·2	+3·2	—
TiO_2	+5·6	nil	—
ZrO_2	nil	—	—
MoO_3	+24·8	+3·2	—
WO_3	+20·8	+1·6	—
Cr_2O_3	+2·4	—	—
U_3O_8	+11·2	<+1·0	—
Co_3O_4	<+1·0	—	—
Fe_2O_3	nil	—	—
ThO_2	<+1·0	—	—
V_2O_5	+13·6	+4·0	—
Fluoride	—	−4·0	nil

EXPERIMENTAL

SUKULU SOILS—

Initially the separation of the niobium by chloroform extraction of its complex with cupferron was attempted, as experience with this type of procedure had been gained during the analysis of uranium - niobium[7] and uranium - titanium alloys.[10] The advantage of this reagent is that the extraction affords a separation from phosphate and is quantitative for small amounts of niobium, as was proved by experiments with carrier-free radioactive niobium-95. However, the large amount of iron is also extracted and a second solvent extraction of niobium as the fluoride with ethyl methyl ketone had to be incorporated, an operation previously used in the analysis of uranium - tantalum and uranium - niobium alloys.[11] Although this double solvent extraction followed by the thiocyanate absorptiometric determination gave good results in about half the time necessary for the Burstall and Williams chromatographic method, it was still considered too time-consuming for routine determinations.

Precipitation of niobium by tannic acid[12] has been in use for many years but no reference was found to its application to determinations of microgram amounts of this element. Preliminary experiments on the recovery of such quantities from weakly acidic solutions containing ammonium oxalate were not encouraging. Tracer niobium was used, and in all these investigations the filtrates from the tannic acid precipitation contained appreciable amounts of niobium. However, with silica as carrier and cinchonine in addition to tannic acid for the precipitation (conditions similar to those used by Schoeller and Jahn[13] for small amounts of tungsten), the filtrates contained considerably less niobium, but the separation was still not quantitative. The simplicity of this procedure was so attractive, in spite of it not being quite quantitative, that it was retained in the final method, with the incorporation of tracer niobium through the whole procedure so that losses could be allowed for.

NIGERIAN GRANITES—

A typical analysis of this material is as follows: SiO_2, 70 per cent.; Na_2O, 5 per cent.; K_2O, 4·4 per cent.; Al_2O_3, 10·5 per cent.; Fe_2O_3, 3 per cent.; FeO, 4·6 per cent.; TiO_2, 0·2 per cent.; ZrO_2, 0·25 per cent.; Nb_2O_5, 0·2 per cent.; and Ta_2O_5, 0·02 per cent.

It is obviously simpler to deal with this material than with the Sukulu soil, and at first it was considered that separation of the niobium could be avoided. While this can be done for head samples, for which a very rapid method becomes possible, difficulty was experienced with some of the mineral-dressing fractions. It was therefore decided to use essentially the same method both for granites and soils and for their mineral-dressing fractions.

The general method in outline is then as follows. The sample is first attacked with sulphuric - hydrofluoric acid, followed by a potassium bisulphate fusion. After dissolving the melt in water, ammonium hydroxide is added, the precipitate that is formed being ignited and fused with sodium carbonate; this triple attack of reagents is necessary to ensure complete solution of the sample and it has therefore been retained in the general method. After the extraction of the melt with water, the niobium is separated by precipitation from slightly acid solution by tannic acid and cinchonine, with silica as carrier, and after ignition of this precipitate, silica is removed by hydrofluoric acid. The residual niobium pentoxide is fused with potassium bisulphate, the melt is dissolved in aqueous tartaric acid, and niobium is determined absorptiometrically with potassium thiocyanate under Freund and Levitt's conditions. As the over-all procedure is not quite quantitative, the necessary correction for losses is determined by incorporation of niobium tracer.

INTERFERING ELEMENTS

Before the above procedure was applied to mineral samples, an investigation was carried out into the behaviour of other elements in the final thiocyanate solution, the investigation being essentially confined to those elements likely to accompany niobium to the final tartrate solution. The following conclusions were reached for the behaviour of iron, tungsten, zirconium and titanium.

IRON—

As iron is a major constituent of Sukulu soils, some of this element passes into the final tartrate solution; the presence of silica with the final niobium tannate precipitate makes it almost impossible to remove the iron completely by washing. According to Freund and Levitt the inclusion of stannous chloride in the thiocyanate solution prevents the interference by iron, but nevertheless this metal causes a small absorption of light, as is shown by the optical density values in Table II. These values were determined on a series of solutions containing increasing amounts of ferric iron in 100 ml of 1 per cent. aqueous tartaric acid. A 10-ml portion of each solution was treated exactly as for the formation of the niobium - thiocyanate colour and the optical density measurements were made at a wavelength of 405 mμ with 4-cm cells.

TABLE II

ABSORPTION OF LIGHT DUE TO IRON

Weight of Fe_2O_3 in 100 ml of tartrate solution, mg..	0	5	10
Optical density	zero	0·023	0·039

The optical density of an iron solution containing 10 mg of Fe_2O_3 was determined at various wavelengths. Similar measurements were also made on a typical niobium - thiocyanate solution and in addition on a blank solution prepared from 10 ml of 1 per cent. aqueous tartaric acid. The results are in Table III and they show that the minimum absorption by iron and the blank is at 430 mμ. The absorption by the niobium complex, however, is so small under these conditions that the use of this wavelength to minimise iron interference is not worth while.

TABLE III

VARIATION OF THE OPTICAL DENSITY WITH WAVELENGTH OF LIGHT

	Optical density at						
	390 mμ	400 mμ	410 mμ	430 mμ	450 mμ	470 mμ	490 mμ
Niobium - thiocyanate complex	0·65	0·59	0·475	0·29	0·185	0·135	0·124
Iron solution	0·047	0·039	0·028	0·024	0·035	0·055	0·064
Reagent blank	0·03	0·02	0·013	0·012	0·025	0·05	0·06

The alternative method was therefore adopted of taking an iron oxide sample through the complete analytical procedure with each batch of Sukulu soils so that the necessary correction for iron could be found and applied.

Optical density readings taken at a wavelength of 405 mμ with a solution containing iron increased with time in accordance with the following results—

Time, minutes	0	15	30	45
Optical density of iron blank	0·015	0·03	0·042	0·05

In contrast the optical density of a niobium - thiocyanate solution remained reasonably constant over this interval of time, as shown by the following results found on a solution containing 40 μg of niobium—

Time, minutes	3	6	8	12	14	16	18
Optical density	0·505	0·538	0·54	0·545	0·54	0·53	0·53

To minimise the interference by iron it is therefore desirable to make optical density measurements about 5 minutes after the formation of the niobium - thiocyanate complex.

TUNGSTEN—

If tungsten is present in mineral samples it is reasonable to expect some of this element to be precipitated with the niobium. Moreover, this element forms a coloured thiocyanate product that causes interference in the determination of niobium pentoxide when the ratio of tungsten trioxide to niobium pentoxide exceeds 1 to 1. A detailed study of the behaviour of this element during the suggested analytical procedure was therefore carried out with the aid of a tungsten tracer and the following distribution of the added activity was found—

Counts per 30 minutes for filtrate from the ammonium hydroxide precipitation = 28,998
Counts per 30 minutes for filtrate from the tannic acid - cinchonine precipitation = 933
Counts per 30 minutes in the final tartrate solution = 31,660

These results show that about 50 per cent. of the tungsten is co-precipitated on the solution being made ammoniacal and, as would be expected, the tannic acid - cinchonine precipitation is very effective for precipitating tungsten from solution. Hence a high proportion of the tungsten accompanying the niobium in the ammonium hydroxide precipitation passes into the final thiocyanate solution. The extent of the interference by tungsten in the determination of niobium pentoxide is shown in Table IV. These values were obtained by adding increasing quantities of tungsten trioxide to 0·2-g portions of a Sukulu-soil sample and then determining niobium pentoxide by the suggested procedure.

Available information indicated that tungsten was not a normal constituent of Sukulu soils or Nigerian granites, but the serious interference caused by tungsten in the thiocyanate method made a fairly rapid test for this element desirable. Moreover, in the event of tungsten being detected, this test should be capable of extension to include its accurate determination. In such circumstances it would then be possible to correct for the absorption due to tungsten, thereby enabling the niobium content to be determined accurately. In the development of this test it was not the intention to apply it to every sample submitted for analysis, but to an occasional sample from each batch.

The spectrographic technique proved too insensitive for the detection of small amounts of tungsten in the residue remaining from the ignition of the tannate - cinchonine precipitate. After a study of possible chemical methods, a suitable technique was developed based on a method for the determination of tungsten in steel that makes use of the sensitive green colour produced with dithiol.[14] In this procedure 10 ml of the final tartrate solution were taken and, after the addition of 2 ml of a mixture of sulphuric - phosphoric acid, were evaporated to fumes. At this stage nitric acid was added to oxidise organic matter (tartaric acid). After the complete removal of nitric acid, the tungsten - dithiol complex was formed and was extracted from solution with amyl acetate. The optical density of this extract was measured with the Spekker absorptiometer and the tungsten content was determined by reference to a calibration graph. Complete details of this test are included in the recommended analytical procedure.

TABLE IV

RESULTS SHOWING THE INTERFERENCE DUE TO TUNGSTEN

Weight of WO_3 added to 0·2 g of Sukulu soil, mg	nil	1	10
Ratio of WO_3 to Nb_2O_5	—	2·18:1	21·8:1
Nb_2O_5 found, per cent.	0·23	0·29	0·50

ZIRCONIUM—

As solutions of Sukulu soils contain phosphate ions, zirconium is likely to accompany niobium to the final thiocyanate solution. However, zirconium with thiocyanate does not produce an interfering colour, even when its concentration is greater than ten times that

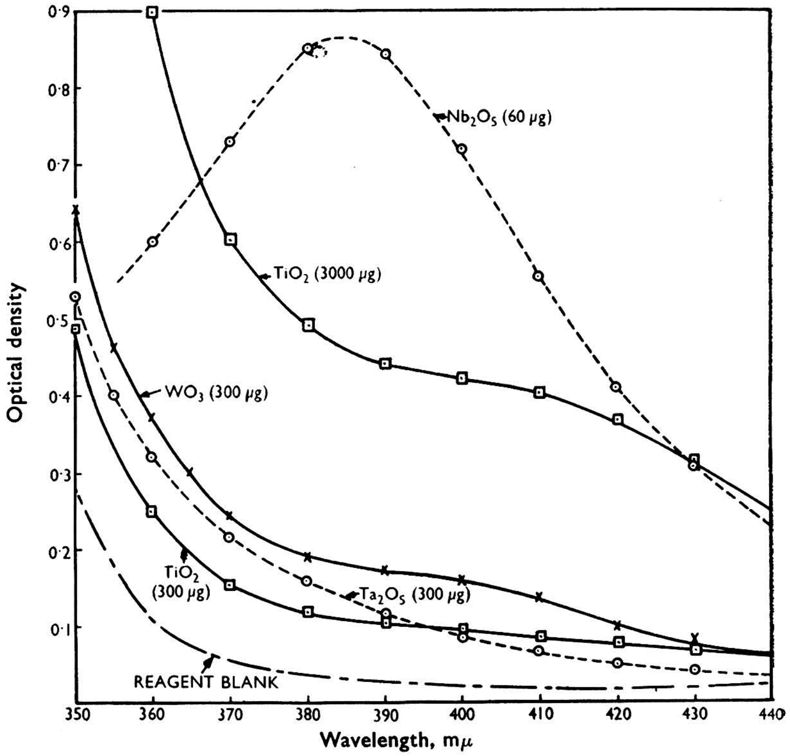

Fig. 1. The variation of optical density with wavelength for different elements in the thiocyanate procedure

of niobium. There should therefore be no interference by this element in the niobium determination. It was confirmed that most of the zirconium accompanied the niobium in the suggested procedure, and the niobium pentoxide values in Table V show that interference by zirconium is insignificant.

TABLE V

RESULTS SHOWING THE NON-INTERFERENCE OF ZIRCONIUM

Weight of ZrO_2 added to 0·2 g of the Sukulu soil sample, mg	0	1·0	10	20
Nb_2O_5 found, per cent.	0·24	0·25	0·25	0·24
Ratio of ZrO_2 to Nb_2O_5	—	~2:1	~20:1	~40:1

TITANIUM—

In Nigerian granites the titanium content is approximately equal to that of the niobium, and interference from titanium is negligible. However, when the ratio of titanium dioxide to niobium pentoxide is 5 to 1 or greater, there is a positive error (see Fig. 1). Several typical Sukulu-soil samples were examined for titanium content by an absorptiometric procedure making use of the colour produced by hydrogen peroxide with titanium in 2·5 *N* sulphuric acid[6] and were found to contain about 1 to 1·5 per cent. of titanium dioxide. Hence the ratio of titanium dioxide to niobium pentoxide in these samples is approximately 5 to 1 or slightly greater. According to the graphs in Fig. 1, optical density measurements at 405 mμ would therefore result in a positive error of about 10 per cent. or more in the niobium determination, owing to the titanium dioxide in the sample.

Although the behaviour of titanium dioxide in the tannic acid - cinchonine precipitation was not studied in very great detail, there was sufficient evidence to indicate that most of this element in the mineral samples passed into the thiocyanate solution. It will be recalled that a wavelength of 405 mμ was chosen for absorption measurements because Freund and Levitt recommended approximately this value for the determination of niobium in the presence of tantalum. As, however, pyrochlore is the only niobium - tantalum bearing material in Sukulu soils, the ratio of tantalum pentoxide to niobium pentoxide is about 1 to 10, and there should be negligible interference from tantalum at a wavelength of 385 mμ, the wavelength corresponding to the peak absorption of niobium thiocyanate. At this wavelength the error caused by titanium dioxide is slightly less than at 405 mμ, and 385 mμ is therefore preferable when a suitable spectrophotometer is available. With the Spekker absorptiometer, however, it is impossible to improve on the earlier recommendation of a mercury-vapour lamp with the filter combination of Wratten No. 2 and Chance OV1. Hence the interference by titanium will be slightly greater with this type of instrument. Even so, the ratio of titanium dioxide to niobium pentoxide in Sukulu-soil head samples containing about 0·2 per cent. of niobium pentoxide is such that the results are high by only about 0·01 to 0·02 per cent. A correction for titanium interference is applicable and details are included in the recommended procedure.

METHOD

Details of the recommended procedure for the determination of niobium pentoxide in Sukulu soils, Nigerian granite and the various fractions produced in the mineral dressing of these materials are as follows.

REAGENTS—

Cinchonine solution—Dissolve 5 g of cinchonine in 100 ml of diluted hydrochloric acid (1 + 1).

Potassium thiocyanate, 3 M—Dissolve 29·0 g of potassium thiocyanate in water and dilute to a volume of 100 ml.

Stannous chloride, 2 M—Dissolve 4·5 g of stannous chloride and a small pellet of tin in 5 ml of hydrochloric acid, sp.gr. 1·16, and then dilute to 10 ml with water.

Acetone—Use AnalaR quality reagent, which should produce no coloration when 10 ml are mixed with a solution consisting of 10 ml of hydrochloric acid, sp.gr. 1·16, 1 ml of 2 *M* stannous chloride and 5 ml of water.

Niobium tracer—Obtain 1 millicurie of carrier-free active niobium-95 dissolved in a few millilitres of 8 *M* hydrochloric acid from the Radiochemical Centre, Amersham. Add to the solution approximately 2 ml of hydrofluoric acid, transfer it to a polythene bottle with water and dilute it to a volume of about 200 ml. Dilute 25 ml of this stock solution to 250 ml in a second polythene bottle for the working solution and store both solutions behind lead or brick shielding.

PROCEDURE—

Weigh 0·200 g of sample (Note 1) into a small platinum dish of 25 ml capacity and add to it about 6 drops of sulphuric acid, sp.gr. 1·84, 3 to 5 ml of water, 5 ml of 40 per cent. w/v hydrofluoric acid and a small volume of tracer solution (Note 2), and evaporate the mixture to fumes of sulphuric acid. Add to the residue a further 5 ml of hydrofluoric acid (Note 3) and again evaporate it to fumes of sulphuric acid.

Heat the dish and contents over a Meker burner to remove all free sulphuric acid and then allow it to cool. Fuse the residue with 2 g of potassium bisulphate and extract the melt with about 100 ml of water. Add ammonium hydroxide solution (1 + 1) to make the solution slightly ammoniacal and leave it warm for 15 to 30 minutes. Filter through a Whatman No. 40 filter-paper and wash the hydroxide precipitate with a cold 1 per cent. ammonium hydroxide solution. Transfer the filter-paper and contents to a platinum crucible and ignite them at a temperature between 600° and 700° C.

Add 2 g of anhydrous sodium carbonate to the crucible and mix it with the oxide residue. Cover the crucible with a platinum lid and fuse the mixture at red heat over a Meker burner for about 15 minutes. Remove the melt from the crucible and then extract it with not more than 100 ml of water in a 250-ml conical beaker. Fuse 100 mg of pure silica (Note 4) with about 0·5 g of anhydrous sodium carbonate in the same platinum crucible. Extract this melt with a small quantity of water, and add the extract to the sample solution. Boil the combined solution, cool it and add 5 g of ammonium chloride and 1 g of tannic acid, with stirring, and then acidify the solution to litmus by the addition of diluted hydrochloric acid (1 + 1) from a burette, adding 5 ml of acid in excess. Next add 5 ml of the cinchonine solution and then two macerated Whatman accelerators. Heat the solution to boiling (Note 5) and continue boiling for about 10 minutes. Then allow it to digest warm for about 1 hour.

Filter the mixture through a paper-pulp pad and wash the precipitate with a 1 per cent. hydrochloric acid solution containing 1 per cent. of cinchonine. Dry and ignite the precipitate in the same platinum crucible at about 700° C. Cool the residue and add 2 or 3 drops of sulphuric acid, sp.gr. 1·84, and about 2 ml of 40 per cent. w/v hydrofluoric acid. Evaporate the solution to dryness and repeat the treatment with hydrofluoric acid to remove silica completely. Then remove the excess of sulphuric acid by fuming. Fuse the residue with 2 g of potassium bisulphate, cool and extract the melt with a solution containing 1 g of tartaric acid (Note 6) in 20 ml of water. Dilute this solution to a volume of 100 ml with water in a calibrated flask (solution A).

With pipettes, place 10 ml of hydrochloric acid, sp.gr. 1·16, 1 ml of 2 *M* stannous chloride and 5 ml of water in a 50-ml calibrated flask. Add 10 ml of acetone, mix the contents thoroughly and cool the mixture to room temperature by immersing the flask in a water-bath for 15 minutes. With a pipette, place 10 ml of solution A, or a suitable dilution of it for samples with high niobium content (Note 7), in the 50-ml flask and, after mixing, add 10 ml of 3 *M* potassium thiocyanate solution. Dilute to the mark with water and after 5 minutes measure the optical density of the solution in a 4-cm cell. For optical density measurements use a spectrophotometer at a wavelength of 385 mμ or the Spekker absorptiometer with Wratten No. 2 and Chance OV1 filters. Correct the optical density readings for each sample for the blank and determine the amount of niobium pentoxide by referring to a calibration graph prepared from a standard niobium solution (see below).

Place 50 ml of the counting standard solution (Note 2) in a beaker and measure its activity with a γ-scintillation counter (Note 8). Replace the solution in the beaker by 50 ml of the sample solution A and repeat the count. Correct all counts for the background count of the instrument. Correct the amount of niobium pentoxide found for experimental losses by multiplying by the factor: counts per minute of the counting standard divided by counts per minute of the sample solution. Finally, calculate the percentage of niobium pentoxide in the sample.

NOTES—

1. For Sukulu soils, weigh 0·2 g of iron oxide into a second platinum dish and take it through the procedure as a blank determination, but do not add niobium tracer.
2. The volume of tracer solution taken should be such as to result in a 50-ml portion of the final tartrate solution giving an activity of a few thousand counts per minute. An equal volume of the tracer solution should also be taken for the counting standard into a 100-ml flask and diluted to the mark with 1 per cent. aqueous tartaric acid solution.
3. It is essential that the tracer niobium should exchange completely with niobium in the sample and this is ensured by the presence of hydrofluoric acid after the niobium mineral has been decomposed.
4. For granites, weigh another 100-mg amount of silica and take it through the rest of the procedure as a blank determination.
5. Care should be exercised here, as the rapid evolution of carbon dioxide may cause loss of solution.
6. For some of the concentrates, it is necessary to use larger amounts of tartaric acid, as follows: 2 g for samples with 4 per cent. of niobium pentoxide; 5 g for those with 15 per cent. of niobium pentoxide.
7.

Approximate Nb_2O_5 content of sample, per cent. ..	1	2	4	16
Dilute a 10-ml sample with 1 per cent. aqueous tartaric acid to	50 ml	100 ml	250 ml	1 litre

8. Gamma-counting is preferable to β-counting because the low energy of the niobium-95 β-particle means low counting efficiency and hence intensification of interference by any β-emitting radiochemical impurity in the niobium-95 tracer solution.

STANDARDISATION PROCEDURE

Preparation of standard niobium solution—Fuse 0·150 g of Specpure niobium pentoxide with 5 g of potassium bisulphate and extract the melt with 200 ml of 5 per cent. aqueous tartaric acid. Dilute the resulting solution to a volume of 1 litre with water and mix the solutions thoroughly. With a pipette, place 10 ml of this solution in a 250-ml calibrated flask and dilute it to the mark with a 1 per cent. aqueous tartaric acid solution. Ten millilitres of this solution contain 60 μg of niobium pentoxide.

Preparation of calibration graph—To each of six 50-ml calibrated flasks add the following: 10 ml of hydrochloric acid, sp.gr. 1·16, 1 ml of 2 *M* stannous chloride, 5 ml of 4 per cent. potassium bisulphate solution and 10 ml of acetone. Mix the contents of each flask thoroughly and then cool them in a water-bath for 15 minutes.

To each flask add suitable volumes of the above standard niobium solution, *e.g.*, 0, 2, 4, 6, 8 and 10 ml and the correct amounts of a 1 per cent. aqueous tartaric acid solution to bring the total volume in each flask to 10 ml. Then add 10 ml of 3 *M* potassium thiocyanate solution to each flask. Dilute the solutions to the calibration mark with water, mix them and measure the optical densities under the conditions described in the procedure. Plot a graph of optical density readings against micrograms of niobium pentoxide.

It is necessary to check the calibration graph with each fresh solution of potassium thiocyanate. This is satisfactorily accomplished by measuring the optical density of a standard solution containing 10 ml of the above niobium solution with each batch of determinations.

TEST FOR TUNGSTEN

REAGENTS—

Sulphuric - phosphoric acid mixture—Mix 15 ml of sulphuric acid, sp.gr. 1·84, with 15 ml of phosphoric acid, sp.gr. 1·75, and dilute to 100 ml with water.

Stannous chloride solution—Dissolve 10 g of stannous chloride in 100 ml of hydrochloric acid, sp.gr. 1·16.

Dithiol solution—Dissolve 1 g of dithiol (3:4-dimercapto-1-methylbenzene) in 100 ml of amyl acetate.

PROCEDURE—

With a pipette, place a 10-ml portion of sample solution A in a 30-ml squat beaker. Add 0·9 ml of sulphuric - phosphoric acid mixture and evaporate to fumes of sulphuric acid. During this evaporation add nitric acid, sp.gr. 1·42, to destroy organic matter and then remove most of the nitric acid by evaporating to fumes of sulphuric acid. After cooling, rinse the beaker with a few millilitres of water and then re-fume to remove nitric acid completely. Cool, add 5 ml of stannous chloride solution and heat the beaker for a few minutes. Then add 10 ml of dithiol solution and digest on a steam-bath for 1 hour with constant stirring.

Cool the solution and transfer it from the beaker to a 25-ml stoppered separating funnel, washing it in with the three separate 2-ml portions of amyl acetate. Run off the aqueous layer and discard it. Add 5 ml of hydrochloric acid, sp.gr. 1·16, to the funnel and shake it well, then allow the liquid to settle and run off the acid layer. Transfer the organic layer to a dry 50-ml calibrated flask, washing it in with three separate 2-ml portions of amyl acetate. Then dilute the solution to volume with amyl acetate and mix it well.

Measure the optical density of this solution with a Spekker absorptiometer, Ilford 608 filters, 4-cm cells and a mercury-vapour lamp. Determine the tungsten content by referring this reading to a calibration graph prepared by applying the above procedure to suitable aliquots of a standard sodium tungstate solution containing 10 μg of tungsten trioxide per ml. Determine the correction to be applied to the niobium thiocyanate reading from a correction graph prepared by applying the thiocyanate procedure to known amounts of tungsten.

TEST FOR TITANIUM

PROCEDURE—

With a pipette, place a 25-ml portion of sample solution A in a dry 100-ml beaker and add 2·5 ml of 18 *N* sulphuric acid. Mix the solutions and cool them. Then add 1 ml of 100-volume hydrogen peroxide, mix the solutions, and measure the optical density. Use the Spekker absorptiometer with a mercury-vapour lamp, Ilford 601 filters and 4-cm cells.

For a blank solution, take another 25-ml portion of sample solution A, add 2·5 ml of 18 *N* sulphuric acid and 1 ml of water. Measure the optical density of this solution. Apply the necessary correction to the optical density reading for the titanium peroxide colour. Determine the titanium concentration of solution A by referring the corrected reading to a calibration graph prepared by applying the above procedure to suitable aliquots of a standard titanium solution. Determine the correction to be applied to the niobium thiocyanate reading from a correction graph prepared by applying the thiocyanate procedure to known amounts of titanium.

Details for the preparation of the calibration graph—Prepare a standard titanium dioxide solution by fusing 50 mg of Specpure titanium dioxide with 1·0 g of potassium bisulphate in a platinum dish. Extract the melt with a 1 per cent. aqueous tartaric acid solution and accurately dilute the extract to 250 ml with the same reagent. For the preparation of the calibration graph take the following volumes of the standard titanium dioxide solution: 0, 2·5, 5·0, 7·5, 10·0, 12·5 and 15·0 ml and make each solution up to 25 ml with the 1 per cent. aqueous tartaric acid solution. Then to each solution add 2·5 ml of 18 *N* sulphuric acid followed by 1 ml of 100-volume hydrogen peroxide. Measure the optical density as above and plot the calibration graph after correcting all readings for the optical density of the solution that does not contain titanium dioxide.

RESULTS

RECOVERY RESULTS FROM SYNTHETIC SOLUTIONS CORRESPONDING TO SUKULU SOILS—

A standard niobium solution was made by fusing 10 mg of Specpure niobium pentoxide with 0·5 g of anhydrous potassium carbonate, extracting the melt with water and finally diluting the solution to 100 ml with water so that 1 ml of this solution contained the equivalent of 100 μg of niobium pentoxide. Volumes of 0, 2, 4, 6 and 8 ml of this standard were added to separate small platinum dishes and evaporated to dryness. As iron is the major constituent in Sukulu soils, 0·2 g of iron oxide was added to each dish and the niobium procedure was applied. The results for the recovery of the niobium are shown in Table VI.

TABLE VI

RESULTS FOR THE ANALYSIS OF SYNTHETIC SUKULU SOILS

Sample	Nb_2O_5 present, %	Nb_2O_5 from optical density measurements, %	Relative γ-activity of final tartrate solution	Corrected Nb_2O_5 found, %
A	0·1	0·07	14,933	0·095
B	0·2	0·15	15,734	0·19
C	0·3	0·23	16,992	0·28
D	0·4	0·29	15,576	0·38
			Standard 20,454	

A qualitative examination of the γ-activity of filtrates and apparatus was carried out to find where losses of niobium were occurring. No activity could be detected in the filtrates from the ammonium hydroxide precipitation, but some was found in the filtrate from the tannic acid precipitation. Most of the niobium was retained in the platinum crucible used for the sodium carbonate fusion step. As much of this niobium is removed by bisulphate fusion, the niobium recovery can be increased by keeping the same platinum crucible for a given sample through the whole procedure. As an example, results of a separate tracer experiment on a typical Sukulu soil, carried out in duplicate as quantitatively as possible, showed 96 and 97·5 per cent., respectively, of the original niobium to be present in the final solution. About 1 per cent. was found in the filtrate from the tannic acid precipitation, the remainder, approximately 3 and 2 per cent., respectively, still being retained by the platinum crucible after the one bisulphate fusion. Hence the method could be applied with reasonable accuracy without tracer niobium, but in rapid routine work much greater convenience results when this technique is incorporated.

ACTUAL SUKULU-SOIL SAMPLES—

The results for various samples of Sukulu soils are shown in Table VII. Tungsten was not detected in any of these samples. This table also includes the results found by a chromatographic[1] and a direct emission spectrographic procedure.[2] The values found by the three procedures can be seen to be in good agreement. Samples 3, 4 and 5 in Table VII were also independently analysed by eight different laboratories that used various procedures in a co-operative scheme organised by the Rio Tinto Co. Ltd. The average results for the niobium pentoxide contents of these samples were reported as 0·163, 0·22 and 0·607 per cent., respectively.

TABLE VII

RESULTS FOR NIOBIUM PENTOXIDE DETERMINATIONS ON SUKULU SOILS

Sample number	Nb_2O_5 by absorptiometry, %	Nb_2O_5 by chromatography, %	Nb_2O_5 content by spectrography (mean values), %	TiO_2 content, %	Ratio TiO_2 to Nb_2O_5 in original sample
1	0·19	0·18	0·19	1·33	7·0:1
2	0·20	0·18	0·18	1·42	7·9:1
3	0·16	0·15	0·14	1·64	10·9:1
4	0·22	0·215	0·19	1·66	7·7:1
5	0·60	0·59	0·56	1·64	2·7:1

SYNTHETIC SAMPLES OF GREATER NIOBIUM CONTENT—

Iron oxide was also used for the preparation of synthetic samples corresponding to the fractions produced by the mineral-dressing treatment of Sukulu soils. The synthetic samples were made from a standard niobium pentoxide solution prepared by the dissolution of 50 mg of niobium pentoxide in 2 ml of 50 per cent. sulphuric acid + 2 ml of hydrofluoric acid, followed by the evaporation of the solution to fumes of sulphuric acid. After cooling,

TABLE VIII

RESULTS FOR THE ANALYSIS OF SYNTHETIC SUKULU-SOIL CONCENTRATES

Nb_2O_5 present, %	Optical density readings corrected for reagent blank	Dilution used for tartrate solution	Readings corrected for sample with zero Nb_2O_5	Nb_2O_5 from optical density readings, %	Relative γ-activity	Corrected amount of Nb_2O_5 found, %
0	0·033	—	—	—	—	—
1	0·334	1 to 5	0·327	0·92	19,070	1·046
2	0·324	1 to 10	0·321	1·80	18,992	2·06
3	0·457	1 to 10	0·454	2·54	17,766	3·10
4	0·245	1 to 25	0·244	3·43	18,176	4·10
					Standard 21,734	

1 ml of hydrofluoric acid was added to the platinum dish and the solution was diluted to a volume of 50 ml with water. Immediately 0, 2, 4, 6 and 8-ml aliquots of this solution were transferred to separate platinum dishes followed by the addition of 0·2-g amounts of iron oxide to each dish. Determinations were then carried out as described in the procedure, and it can be seen from the values in Table VIII that the niobium pentoxide content found is in close agreement with that present.

MINERAL-DRESSING SAMPLES FROM SUKULU SOILS—

After the satisfactory results for the synthetic samples, the procedure was applied to samples produced during the mineral-dressing treatment of Sukulu soils. These samples were also examined by the direct spectrographic procedure; the agreement between the determinations of most of the niobium pentoxide contents was good, as is shown by the results in Table IX.

TABLE IX

RESULTS FOR NIOBIUM PENTOXIDE DETERMINATIONS ON MINERAL-DRESSING SAMPLES

Sample number	Nature	Principal minerals by X-ray analysis	Nb_2O_5 by absorptiometry, %	Nb_2O_5 spectrographically (mean values), %	TiO_2 content, %
1	Pyrochlore concentrate	Apatite (strong) Magnetite (strong) Pyrochlore (medium) α-Quartz (weak)	4·11	4·17	1·82
2	Apatite concentrate	Apatite (strong) α-Quartz (weak) Other phases very weak	0·94	0·96	—
3	Apatite concentrate	Same as 2	2·51	2·44	2·44
4	Apatite middlings	Apatite (strong to medium) α-Quartz (strong) Other phases very weak	0·88	0·86	1·44
5	Apatite middlings	Same as 4	0·27	0·26	—
6	Tailings	α-Quartz (strong) Other phases weak or medium	0·14	0·13	0·7
7	Tailings	Same as 6	0·26	0·29	—
8	Tailings	Same as 6	0·14	0·10	—

NIGERIAN GRANITES—

Head materials—The absorptiometric procedure was applied to several typical head samples of Nigerian granite, the iron blank being replaced by a silica blank. These samples were also examined by the direct spectrographic procedure. As shown in Table X, the agreement was good for the niobium pentoxide results by both methods.

TABLE X

RESULTS FOR NIOBIUM PENTOXIDE DETERMINATIONS ON NIGERIAN GRANITES

Sample number	Optical density readings corrected for silica blank	Nb_2O_5 content from optical density readings, %	Relative γ-activity	Corrected Nb_2O_5 content, %	Nb_2O_5 spectrographically (mean values), %
Granite 1	0·303	0·181	12,158	0·21	0·20
Granite 2	0·283	0·169	12,186	0·196	0·19
Granite 3	0·323	0·193	11,952	0·23	0·25
			Standard 14,140		

Mineral-dressing samples—Practical application of the method was tested by examining samples from a complete mineral-dressing experiment on Nigerian granite. The various concentrates and tailings were weighed and also examined for niobium pentoxide content. Table XI contains the results of this experiment and it will be seen that the calculated niobium pentoxide content (0·224 per cent.) for the head sample is in good agreement with the value found (0·22 per cent.). This agreement shows that the niobium pentoxide values for the different concentrates and tailings are satisfactory and that the recommended procedure is suitable for all types of samples produced in the mineral-dressing treatment of Nigerian granites.

TABLE XI

RESULTS OF A MASS BALANCE TEST CARRIED OUT ON A NIGERIAN GRANITE SPECIMEN

Nature of fraction	Weight, %	Nb_2O_5 content by absorptiometric procedure, %	$\frac{\text{Weight, \%} \times Nb_2O_5\text{, \%}}{100}$
Pyrochlore concentrate	0·83	15·67	0·1300
Cryolite concentrate (essentially cryolite) ..	2·25	0·60.	0·0135
Cleaner tails (mainly quartz and riebeckite)..	1·71	0·31	0·0053
Recleaner tails (mainly quartz and riebeckite)	0·18	0·74	0·0013
Slimes (similar to original ore)	11·95	0·22	0·0263
Rougher tails (mainly quartz and riebeckite)	83·08	0·057	0·0474
	100·0		0·2238
			Calculated head = 0·224 per cent. of Nb_2O_5

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The Absorptiometric Determination of Niobium in Low-grade Ores

By A. E. O. MARZYS

(*Presented at the meeting of the Society on Wednesday, November 4th,* 1953)

The absorption of light in the near ultra-violet by the reduced niobium - thiocyanate complex in an organic medium is made a basis for the determination of niobium in low-grade ores and minerals. The respective merits of a water - acetone mixture and of ether as solvents are described. The method has been adapted for use with a Hilger Spekker absorptiometer provided with a mercury-vapour lamp. Four modifications of the main procedure are described for use in the presence of certain interfering elements.

The results for a variety of African soils and minerals are compared with those found by gravimetric methods. The precision of the method is as good as, and probably better than, that of gravimetric methods when applied to complex soils and rocks of low niobium content. The speed and ease of manipulation are greatly increased.

By suitable adjustment of the amounts of material used, the method can, in the absence of vanadium, be extended to all niobium minerals. The ratio of niobium to tantalum in mixed oxides can be rapidly found by determining niobium and titanium colorimetrically and calculating the tantalum content by difference.

THE growing importance of niobium in the development of the jet-engine industry and the scarcity of its sources has in recent years directed attention to the low-grade niobium-bearing minerals, in particular those in various parts of Africa. As their exploration was undertaken, there was a need for a fairly accurate method for the determination of niobium in complex minerals and soils that would yield results in less time than those based on gravimetric analysis.

During a discussion held in the course of the International Congress of Analytical Chemistry in Oxford, 1952, several speakers stressed the fact that the absence of a suitable rapid method had held up prospecting and development schemes for niobium minerals.[1] During the same discussion, it was rightly stressed that titanium presented the greatest problem in the determination of tantalum and niobium in minerals as it was always found in association with these elements. Pyrochlore, which was likely to become an important ore of niobium, was nearly always accompanied by highly titaniferous material. With these facts in mind, the present work was undertaken with the object of finding an analytical method of a routine type in which speed and ease of operation would be the main considerations, while a fair standard of accuracy was retained. It was desired to make the method suitable for use in small laboratories attached to the mineral development establishments.

In choosing a suitable procedure, all gravimetric methods had to be eliminated as they necessarily involved rather lengthy chemical separations. The majority of the methods used are based on the work of Schoeller and co-workers[2] from 1921 onwards. Various modifications of the basic procedures have been tried with the object of improving speed. However, in view of the complexity of the materials dealt with, no modification afforded an appreciable reduction in the time needed.

Volumetric procedures[3] involving the reduction of niobium offered neither improved rapidity nor the solution of the titanium problem. The same could be said about the electro-reduction procedure followed by the colorimetric determination that was used by Tomiček and co-workers.[4,5] Meimberg's[6] reduction of fluoride with zinc leads to serious etching of the glass cells and is subject to interference from titanium.

The necessity for setting up special apparatus precluded the possibility of determining niobium on a batch system by chlorination.[7] Useful chromatographic work carried out at the Chemical Research Laboratory, D.S.I.R., at Teddington,[8] provided a method of clear-cut separation and determination of niobium and tantalum but, when applied to the low-grade ores, the need for carrying out preliminary chemical separations lengthened the procedure beyond the time so far required for the gravimetric determinations.

Turning to the colorimetric and related procedures, the scarcity of suitable reagents for niobium was revealed. The two most frequently used have been hydrogen peroxide[9] and pyrogallol.[10]

The usefulness of hydrogen peroxide has been considerably extended recently by the study of the absorption spectra of perniobic acid by Telep and Boltz,[11] who found that maximum absorption occurred in the ultra-violet region at 342 mμ. In spite of that, the method remained comparatively insensitive while being subject to many interferences and, furthermore, it involved working in almost concentrated sulphuric acid solutions. As for pyrogallol and the related pyrocatechol tried out by Tomiček and Jerman,[5] the correction for titanium frequently exceeded the absorption due to niobium, which was found not to follow Beer's law exactly. These reagents, therefore, while remaining virtually the only reagents for tantalum, were of very limited value for niobium in titaniferous material. Also the molybdate reagent used by Davidov, Vaysberg and Burkser[12] had to be rejected because absorption due to titanium was much greater than that due to niobium. Hydroquinone, which was used by Johnson[13] in steel analysis, proved unsuitable for similar reasons.

The present work is based on the observation first made by Alimarin and Podvalnaya[14] that a niobium solution when treated with stannous chloride formed a yellow complex with acid thiocyanate, the colour being enhanced in an organic medium. The absorption behaviour of the complex and the factors influencing the development of colour have been thoroughly studied by Lauw-Zecha, Lord and Hume[15] and by Freund and Levitt.[16] This reagent was found to be by far the most sensitive one so far used for niobium. At the time of submitting this paper for publication no results of the application of the reaction to mineral analysis had appeared in the literature, although a mention was made by Milner[1] that he and Smales were working on the problem.

While Lauw-Zecha *et al.* used ether as the solvent medium, Freund and Levitt studied absorption in an acetone - water mixture. Both procedures were found to possess certain merits and disadvantages, depending in particular on the materials analysed, as described in the following pages. Both groups of authors used spectrophotometers and found the absorption peak lay in the ultra-violet region at 385 mμ. In the present work an adaptation was made for the use on a simple filter-type absorptiometer such as the Hilger Spekker, type H 760.

EXPERIMENTAL

APPARATUS—

Photo-electric absorptiometer—The maximum absorption of the niobium - thiocyanate complex occurs, according to the two papers quoted,[15,16] in the ultra-violet region of 385 mμ. For maximum sensitivity, therefore, an ultra-violet spectrophotometer such as the Beckman model DU or B, Hilger and Watts Uvispek or Cambridge Unicam SP 500 should be used. However, it was the express purpose of this work to investigate the possibility of using a filter-type absorptiometer which, unlike the more expensive spectrophotometers, is found in almost every analytical laboratory. For this purpose, the Hilger Spekker absorptiometer type H 760, provided with a mercury-vapour lamp, was found to be suitable. The two lines emitted by the mercury-vapour lamp in the near ultra-violet region, at 405 and 365 mμ, were isolated by means of the following filters: Wratten No. 2 and Chance OV1 for 405 mμ and Wood's glass filters for 365 mμ. The Calorex heat filters were left in their mounts during all determinations and, while slightly reducing total transmission, they were found to increase the optical density readings.

Spectrophotometer—A Cambridge Unicam SP 500 spectrophotometer was used for checking the absorption spectra.

Glassware—All glassware used was of Pyrex glass.

Crucibles—Silica crucibles were used for fusions of all materials except the highly siliceous ores when platinum crucibles were used.

Centrifuge—George and Becker standard type A1321–1.

REAGENTS—

All reagents were of analytical-reagent grade. The niobium pentoxide used as standard was Specpure material J.M.605 supplied by Johnson Matthey & Co. Ltd.

OUTLINE OF THE PROCEDURES USED—

The niobium minerals investigated ranged from high grade columbite - tantalite to phosphatic soils containing 0·1 per cent. of niobium pentoxide, and they included such minerals as microlite with about 72 per cent. of tantalum pentoxide and 0·6 per cent. of niobium pentoxide, and granite with pyrochlore occlusions amounting to about 0·2 per cent. of niobium pentoxide. Most of the materials available were ferruginous and phosphatic soils containing a high proportion of substances soluble in dilute hydrochloric acid. As it had been shown from long experience with those soils that pyrochlore was completely unaffected on warming it with dilute hydrochloric acid, 1-g samples were leached with diluted hydrochloric acid (1 + 2), the residue was filtered, washed with hot dilute hydrochloric acid and ignited. This treatment left only small amounts of iron and phosphate in the residue that were insufficient to cause significant interferences in the procedures used. Fluorides were then expelled by heating the residue to dryness with a few drops of concentrated sulphuric acid. For samples of highly siliceous materials, such as Nigerian granite containing 70 per cent. of silica, the silica was removed by heating it with hydrofluoric acid and a few drops of concentrated sulphuric acid. The residues were fused with bisulphate and extracted with aqueous tartaric acid. The insoluble residue, if any, was filtered off or centrifuged. Aliquots of the solutions prepared in this way were treated with stannous chloride, hydrochloric acid and potassium thiocyanate. The optical density was measured either in a homogenous water - acetone medium or in an ether extract. It was found convenient to combine stannous chloride and hydrochloric acid in one solution and, in the first procedure, potassium thiocyanate was used in water - acetone solution (1 + 1). The second procedure was found to be preferable in the presence of uranium and small quantities of copper, whose complexes with thiocyanate are not extracted with ether. As it was three times as sensitive as the acetone procedure, it was more satisfactory for very low concentrations of niobium. Molybdenum, mercury and larger amounts of copper, if present, were conveniently removed by precipitation with hydrogen sulphide. Vanadium was separated by pyrosulphate - tannic acid precipitation and a method of correcting for tungsten was worked out. In fact, the last five metals were not found in the minerals available, except for insignificant amounts of tungsten in the Nigerian granite. For greatest accuracy a very small correction for titanium, never exceeding 1 per cent. of the total reading, could easily be applied.

DEVELOPMENT OF COLOUR AND ABSORPTION BEHAVIOUR—

The depth of the yellow colour of the niobium - thiocyanate complex is greatly enhanced by the presence of an organic solvent, the maximum absorption occurring at about 385 mμ. It was found, on checking the absorption curves with the aid of the Unicam spectrophotometer, that the loss of sensitivity brought about by measurements of optical density at 365 or 405 mμ (the two wavelengths available with a Hilger Spekker absorptiometer) would be 10 to 20 per cent. The two ultra-violet lines emitted by the mercury-vapour lamp are almost equidistant from the maximum-absorption wavelength and it could be expected that the extinction would be identical for both. This was found to be only approximately true. Owing to the slight shift of the absorption curve, depending on the medium used and to the non-symmetrical shape of the peak, the optical density readings were higher for the 365 mμ than for the 405 mμ wavelength when the water - acetone medium was used, while the reverse was true for the ether-extract medium. This is shown in Figs. 1 and 2, where also the curve for 436 mμ obtained with a tungsten lamp and Kodak No. 543 violet filters, is drawn for comparison. It can be seen on comparing the figures in the tables that Beer's law is obeyed better in the ether medium, which also affords a sensitivity almost three times greater than the acetone - water (1 + 4) medium.

In selecting the most suitable wavelength to use, it was found that the optical density readings at 405 mμ reached a maximum almost immediately and remained practically unchanged for at least 30 hours. Absorption at 365 mμ developed more slowly and continued to increase during about 6 hours. A slight fall in absorption was then always observed. Thereafter the absorption continued to increase steadily. For this reason, in spite of the greater sensitivity attainable with acetone at 365 mμ, 405 mμ was selected; with the ether-extraction procedure, the latter wavelength was better from both points of view. The reason for the increase in absorption at 365 mμ becomes obvious on inspecting the absorption spectrum recorded with the Unicam spectrophotometer, as shown in Fig. 4, where the polymerisation or decomposition processes of the thiocyanic acid caused the absorption due to complex formation, as measured against the reagent blank, to increase with time at below 385 mμ. It is seen that there may be a definite advantage in working at a wavelength somewhat higher than that of the maximum absorption at 385 mμ.

In all determinations a steady increase in the blank absorption on standing was observed

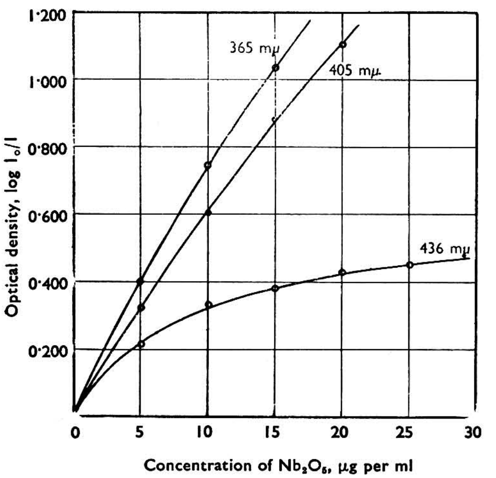

Fig. 1. Calibration graphs at three different wavelengths in water - acetone medium

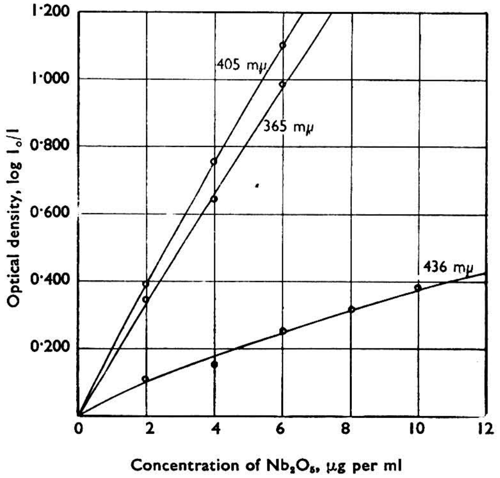

Fig. 2. Calibration graphs at three different wavelengths in ether extract

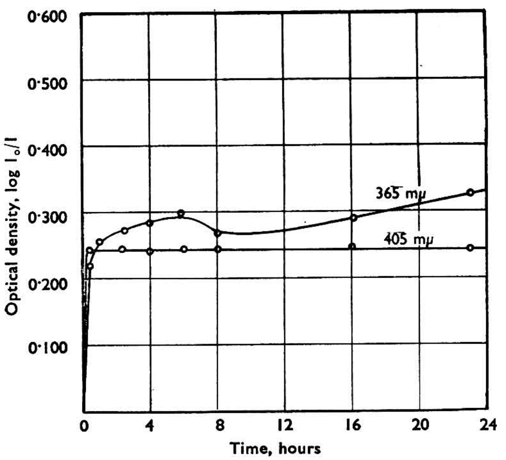

Fig. 3. Stability of colour in water - acetone medium of a solution of a Sukulu soil containing 2·9 μg of Nb_2O_5 per ml

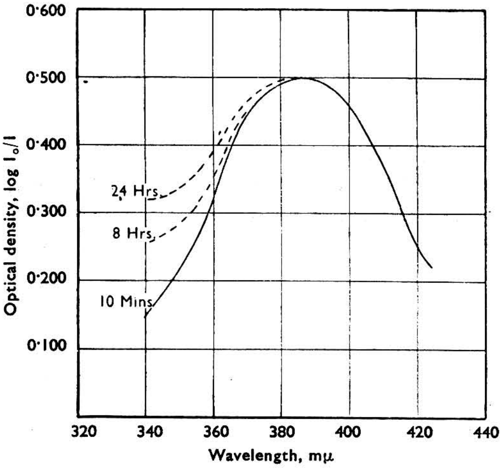

Fig. 4. Variation with time of the absorption spectrum of the niobium - thiocyanate complex in water - acetone medium

Factors affecting the degree of absorption

The reactions leading to the formation of the coloured thiocyanate complex were found to be very susceptible to variations in the quantity and quality of the reagents added and to changes in the procedure.

The reagents causing an increase in the colour intensity are, in the order of decreasing effectiveness, acetone (or ether), thiocyanate, hydrochloric acid and stannous chloride. Tartaric acid and sulphate suppress the colour, but this effect is lessened by the action of the organic medium in preventing their ionisation.

When comparing optical densities with a calibration graph or with the standards, it was found necessary to adhere very strictly to the amounts recommended in the method. When calculating the proportions of various reagents to be used, it was obviously advantageous from the point of view of sensitivity to use as large a proportion as possible of the first group of reagents and to keep the tartrate and sulphate concentrations at a minimum. The main limiting factor in the first case was the point at which precipitation started. Apart from that, however, it was found that too great an excess of thiocyanate and of hydrochloric acid reduced the stability of the complex and led to poor reproducibility of the results. Acetone, alternatively, afforded a considerable enhancement of the colour, as well as an improvement of reproducibility right up to the precipitation point. Unfortunately, an unexpected factor intervened. It was found that doubling the amount of acetone from 10 to 20 ml per 50 ml of solution caused the optical density of the niobium complex to be increased about 2·5 times, but the optical density due to titanium, which is present in all niobium minerals, was increased six times for the 365-mμ wavelength and not less than fifty times for the 405-mμ wavelength. There was also a slight shift of the absorption peak towards a longer wavelength. It was desired to ensure that, for amounts of titanium ten times greater than the niobium, the absorption due to titanium should not exceed 1 per cent. of that due to niobium; in this way the correction could be dispensed with in routine work. For this purpose it was found necessary not to exceed a 20 per cent. content of acetone in the final coloured solution.

Contrary to what could be inferred, the rapid increase of titanium absorption did not persist in the wholly organic medium. With the ether-extraction procedure the original yellow colour due to titanium faded after a few minutes, and it amounted to only about one-third of that in 20 per cent. acetone and in this solvent the titanium correction was always negligible.

Stannous chloride enhanced the niobium and titanium colours to an approximately equal extent.

Sulphate and tartaric acid not only suppressed the colour slightly but, when present in increased concentrations, caused a slow crystallisation of acid tartrates in the original solution, thus reducing the strictly fixed amount of sulphate and tartrate in solution. Their quantities have, therefore, been reduced to a minimum consistent with an adequate amount of potassium bisulphate for fusion and a tartrate concentration that is sufficient to prevent hydrolysis. Sodium bisulphate appears to be better than potassium bisulphate for the fusion. In minerals in which tantalum exceeds about 25 per cent. of the mixed earth-acids, it is better to maintain an increased tartrate concentration. (Hydrolysis of tantalum leads to loss of niobium by adsorption on the basic salt.)

The best order for adding the reagents to the sample was found to be stannous chloride in hydrochloric acid and then thiocyanate in water - acetone solution. Potassium and ammonium thiocyanates were found to give identical absorptions when present in the same molecular proportions. Potassium thiocyanate was found to be more convenient to use, as it is less hygroscopic and consequently can be weighed out more accurately, especially in a tropical climate with a high relative humidity. Thiocyanate solutions, especially those of the ammonium salt, were found to age quickly. After standing for 1 day, a solution of potassium thiocyanate showed a 3 per cent. decrease in the optical density of the niobium complex produced with it. After 1 month the decrease was 60 per cent. It was found necessary to prepare the thiocyanate - acetone solution freshly every day.

The stannous chloride solutions in concentrated hydrochloric acid were found to be quite stable. Standard solutions were prepared by fusing niobium pentoxide with potassium bisulphate and dissolving the melt in 7·5 per cent. aqueous tartaric acid. These were stable for up to a fortnight; after 3 weeks, a 1·8 per cent. decrease in concentration of the solution was observed.

In view of the great influence exerted on the depth of colour by all the reagents and especially by the thiocyanate solutions, it was found advisable to standardise the method by determining the optical density of two or three aliquots of the standard niobium solution concurrently with each group of samples, a fresh thiocyanate solution being used. The readings were used to check a calibration graph, or the results could be calculated from the standard aliquot closest in niobium pentoxide content to the sample under consideration.

Most of the work was carried out at a room temperature of 27° to 29° C; it was found that temperature did not have an appreciable influence on colour intensity at between 20° and 32° C. The prevailing room temperature introduced a handicap into the ether-extraction modification, as it was very near the boiling point of ether. No similar solvent was, however, found to be convenient.

If the solutions were kept in securely stoppered flasks and the optical density readings were carried out quickly, reasonable precision was attained. Nevertheless, it constituted one more point in favour of the acetone - water modification, which was used whenever possible, except where specified below.

INTERFERENCES—

A fairly thorough study of interferences for the two proposed procedures was carried out by the authors of the two papers quoted.[15,16] In the present work the study was confined to those ions that are likely to be present in the niobium-bearing minerals and to working out modifications to the proposed procedure, which would make possible the determination of niobium in the presence of the interfering elements.

The most serious interference is obviously caused by the metals for whose determination the thiocyanate method is used and whose maximum absorption peaks lie near 385 mμ. These are as follows (the maximum absorption wavelengths are approximate and apply to the acetone - water procedure)—

Iron	480 mμ
Rhenium..	432 mμ
Tungsten	420 mμ
Uranium	375 mμ

In addition to these, Crouthamel and Johnson[17] give the absorption curves of several other metals possessing maxima at the following wavelengths—

Cobalt	335 and 630 mμ
Chromium	about 600 and 400 mμ
Copper	320 mμ
Lead	320 mμ
Nickel	400 and 340 mμ

The degree of interference caused by those and some other ions likely to be found in niobium minerals is shown in Table I. The results were determined by the acetone - water procedure.

TABLE I

THE EFFECT OF VARIOUS IONS ON THE DETERMINATION OF NIOBIUM IN WATER - ACETONE MIXTURE AT 405 mμ

Interference expressed as	Percentage error when weight ratio of interference to Nb_2O_5 is—		
	1:1	10:1	100:1
CuO	Precipitation	Precipitation	Precipitation
TiO_2	0	+1	+108
ZrO_2	−0·3	−1·3	−2·3
V_2O_5	+47·5	—	—
Ta_2O_5	0	−15	−25
MoO_3	+4	+8	+105
WO_3	+38	+190	—
U_3O_8	−15	−3	+42
ThO_2	+6	−5	−13
Fe_2O_3	0	+0·4	+22
NiO	+9	+22	+174
Co_3O_4	−2	0	+7
Cr_2O_3	−5	−1	+36
PtO_2	+8	+61	Precipitation
F	−4	−15	—
P_2O_5	0	0	−2

The methods of dealing with the interferences set out in the table were divided into the following groups—

I. Interferences considered as insignificant in the acetone - water procedure as described below:
   Zirconium, cobalt and tantalum in concentrations lower than niobium.

II. Interferences reduced to insignificant proportions by the pre-treatment in the general method:
   Fluoride, phosphate, iron, lead and barium (precipitated and removed as sulphate).

III. Interferences removed by chemical separation:
    Copper, mercury, molybdenum, platinum and vanadium.
IV. Interferences minimised by using the ether-extraction procedure:
    Uranium, chromium, nickel, thorium, copper and tantalum (in large quantities).
V. Interferences dealt with by applying a correction:
    Tungsten and titanium.

Rhenium was left out of consideration as it is most unlikely to be found with niobium.

Taking these groups separately, the methods adopted were as follows.

GROUP II—

A primary leach with diluted hydrochloric acid (1 + 2) reduces any phosphate and iron present in the sample to insignificant proportions in most of the minerals used. The niobium content was never found to be affected. Stannous chloride suppresses the interference of the residual iron. If large amounts of insoluble iron are present, a good method of separating it was found in replacing the bisulphate fusion by a potassium or sodium hydroxide fusion in a silver crucible and filtering and neutralising the filtrate containing niobium with the sulphuric acid. This treatment was also found to separate a part of the titanium.[18] Contrary to the findings of Alimarin and Podvalnaya,[14] repeated by Lauw-Zecha *et al.*, the faint orange colour given by large amounts of iron was completely extracted by ether, as was that given by vanadium. Fluoride was expelled completely in the pre-treatment by ignition with a few drops of sulphuric acid.

GROUP III—

Copper, mercury and platinum are easily removed with hydrogen sulphide. Complete removal of small amounts of molybdenum by simple precipitation with hydrogen sulphide presents well-known difficulties, although Geld and Carroll[19] used this method in their determination of niobium and tungsten in alloys. A very satisfactory precipitation method with thiosulphate and hypophosphite recently described by Rây[20] was found to cause co-precipitation of niobium by hydrolysis. The use of antimony as carrier, as described by Henrickson and Sandell,[21] turned out to be the best way. Passing hydrogen sulphide for 5 minutes under slight pressure into a tartaric acid extract of the bisulphate melt precipitated all the molybdenum and antimony without affecting the niobium (see Table II). The precipitate was easily removable by filtration.

TABLE II

SEPARATION OF MOLYBDENUM FROM NIOBIUM BY HYDROGEN SULPHIDE BY MODIFICATION 1 TO THE MAIN PROCEDURE

Nb_2O_5 taken, mg	MoO_3 taken, mg	Nb_2O_5 found, mg
0·80	—	0·79
0·80	0·80	0·78
0·80	8·00	0·81
0·40	—	0·40
0·40	0·80	0·41
0·40	8·00	0·41

The method is not applicable in the presence of vanadium, when classical methods of separation must be used.[2]

GROUP IV—

Uranium forms a strongly coloured yellow complex with thiocyanate in water or water - acetone mixtures. On shaking the aqueous solutions of the mixture with ether, it was found that the colour faded until both layers became colourless. On the addition of more thiocyanate to the aqueous layer, the colour returned to its previous strength, but it disappeared again on shaking. It was concluded that ether withdrew the thiocyanate ion from the complex, leaving all the uranium in the water layer. In this way the ether-extraction procedure affords an excellent way of determining niobium in the presence of uranium.

Copper formed a precipitate of cuprous thiocyanate that floated on the water - ether interface. Small amounts of copper could be separated by extraction with ether of the niobium complex, but, for larger amounts, copper must be separated by means of hydrogen sulphide.

The error caused by tantalum in acetone - water mixture containing amounts of tantalum pentoxide up to twice those of niobium was negligible; above a ratio of tantalum pentoxide to niobium pentoxide of 50 to 1 the error reached a constant value of almost −25 per cent. Between those values extraction with ether provided a means of reducing the error. With tantalum minerals containing very little niobium, *e.g.*, microlite, a reliable estimate was made by adding 33 per cent. of the determined value to the result. Coloured solutions given by nickel, chromium, thorium and cobalt were not extracted by ether, the error being thereby reduced to negligible proportions.

GROUP V—

Tungsten forms a yellow complex in all media tried, including water. The absorption of the niobium complex in water is very weak. Geld and Carroll[19] determined tungsten by thiocyanate in the presence of niobium by first boiling their sample solution with stannous chloride for a minute, cooling it and then adding the thiocyanate solution to it. In this way, according to them, the interference by niobium was completely eliminated, while the precision of tungsten determinations was greatly increased. This was found to be only partly true. The absorption due to niobium was not completely eliminated, but only diminished by about 50 per cent. at 405 mμ, at which wavelength tungsten gave maximum absorption in the Spekker absorptiometer; that due to tungsten was in fact increased and stabilised. By taking readings at 436 mμ it was possible to obtain the optical density due to tungsten alone, as niobium did not interfere at all at this wavelength. A correction could then be made from a calibration graph.

The effect of titanium was partly dealt with in the preceding paragraph. A correction is easily made by determining the amount of titanium with hydrogen peroxide and subtracting it from the total thiocyanate reading, with the aid of a correction graph (Fig. 5). The correction for the titanium dioxide to niobium pentoxide ratio of 10 to 1 was about 1 per cent. with the acetone procedure and about 0·3 per cent. with the ether procedure. For most routine purposes, it could, therefore, be omitted.

METHOD

REAGENTS—

Standard niobium solution—Fuse 0·0250 g of Specpure niobium pentoxide (J.M.605) with 5 g of fused sodium bisulphate. Extract the melt by heating it with 10 per cent. tartaric acid over a small flame, cool the solution and make it up to 250 ml with 10 per cent. tartaric acid. Then 1 ml contains 0·1 mg of niobium pentoxide.

Tartaric acid, 10 *per cent.*—Dissolve 100 g of the acid in water and dilute to 1 litre.

Bisulphate - tartaric acid blank solution—Dissolve 20 g of fused sodium bisulphate and 100 g of tartaric acid in water and dilute to 1 litre.

Stannous chloride solution in concentrated hydrochloric acid—Warm 50 g of stannous chloride, $SnCl_2.2H_2O$, with about 250 ml of concentrated hydrochloric acid (32 per cent.; analytical-reagent quality) for a few minutes until the solution is clear. Cool and make up to 500 ml with concentrated hydrochloric acid.

Thiocyanate - acetone solution—Weigh out as quickly and as accurately as possible 72·9 g of analytical reagent quality potassium thiocyanate or 57·1 g of ammonium thiocyanate. Place a funnel in the neck of a 500-ml flask, transfer the thiocyanate to the funnel and pour 250 ml of acetone through it. Wash the remaining crystals through with water, shake the flask until they have dissolved, and make up to 500 ml. Make a fresh solution every day.

Aqueous thiocyanate (*for the ether-extraction modification*)—Dissolve 72·9 g of potassium thiocyanate or 57·1 g of ammonium thiocyanate in water and dilute to 250 ml.

Standard titanium solution—Prepare a solution containing 0·1250 g of Specpure titanium dioxide (J.M.435) in 250 ml of 10 per cent. tartaric acid by the methed described for the standard niobium solution.

Sulphuric acid, diluted (1 + 1, *v*/*v*).

PROCEDURE—

Weigh out exactly 1·0000 g of finely ground material into a 250-ml beaker. Add 30 ml of concentrated hydrochloric acid and 60 ml of water and cover the beaker with a clock-glass. Simmer gently for half an hour on a hot-plate. Filter hot through Whatman No. 40 or No. 540 filter-paper and wash thoroughly with hot dilute hydrochloric acid. Ignite the residue in a silica crucible, or a platinum crucible for materials rich in silica. Add 3 drops of concentrated sulphuric acid, evaporate and ignite over a small flame to remove fluorides. If the sample is in a platinum crucible, add 3 drops of sulphuric acid, fill one-third full with 40 per cent. hydrofluoric acid and evaporate to dryness, then expel sulphur trioxide by heating.

Fuse the residue with exactly 2 g of fused sodium bisulphate and extract the melt with 10 per cent. aqueous tartaric acid in the manner described for the preparation of standard niobium solution, using a 100-ml beaker. Filter if necessary, wash and make up to 100 ml with 10 per cent. aqueous tartaric acid.

Alternatively, make up to 100 ml without filtering and centrifuge a portion for 5 minutes at 2000 to 3000 r.p.m. at 13 cm radius.

Development of colour—With a pipette, place a 10-ml aliquot in a 50-ml calibrated flask. For samples with a niobium pentoxide content exceeding 0·5 per cent., take a smaller aliquot and add an appropriate amount of blank solution containing sodium bisulphate and tartaric acid so as to make a total of 10 ml of solution. Add 10 ml of stannous chloride and 20 ml of thiocyanate - acetone solution, both from burettes. Dilute almost to the mark and cool under a tap for 15 minutes. Make up to the mark exactly and determine the absorption at 405 mμ with a Spekker type H 760 absorptiometer with a mercury-vapour lamp and Wratten No. 2 and Chance OV1 filters (Calorex heat filters remaining in the mounts). Use 1-cm cells and a blank containing 10 ml of tartaric acid - bisulphate solution and the other reagents.

At the same time, read the absorption values for solutions containing 3, 6 and 9 ml of standard niobium pentoxide solution, made up to 10 ml with the tartaric acid - bisulphate solution and the appropriate amounts of the other reagents, as used for the sample solutions. The three points should give an almost straight line on a graph.

Titanium correction—With a pipette, place a 10-ml aliquot of the sample solution in a 50-ml flask. Add 2·5 ml of syrupy phosphoric acid, 10 ml of diluted sulphuric acid (1 + 1) and 5 ml of 20-volume hydrogen peroxide. Dilute almost to the mark, cool, make up exactly to the mark and determine the absorption at 405 mμ with a mercury-vapour lamp against a blank in which 10 ml of bisulphate - tartaric acid solution has been used. The 2-cm cells are used. The reading obtained is marked on a titanium dioxide - hydrogen peroxide graph (Fig. 5)

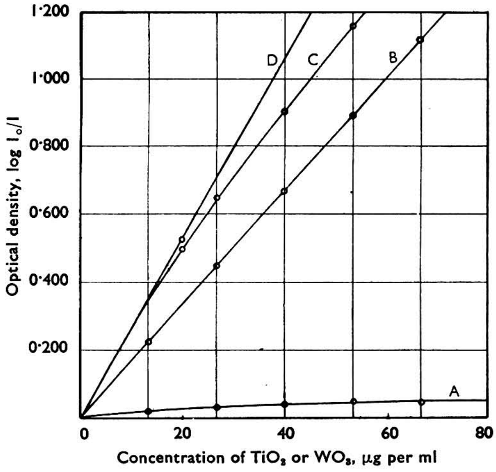

Fig. 5. Correction graphs for titanium and tungsten. Graph A, titanium with thiocyanate in acetone - water medium at 405 mμ, 1-cm cells; graph B, titanium with hydrogen peroxide at 405 mμ, 2-cm cells; graph C, tungsten with thiocyanate in water at 436 mμ, 4-cm cells; graph D, tungsten with thiocyanate in acetone - water medium at 405 mμ, 1-cm cells

and a vertical line is drawn to the intersection with the titanium dioxide - thiocyanate graph, from which the correction to be subtracted from the niobium pentoxide reading is found.

Calibration graph for titanium correction—Use 4, 8, 12 and 16-ml aliquots of the standard titanium solution and develop the colour (*a*) with stannous chloride - thiocyanate and acetone and (*b*) with hydrogen peroxide, phosphoric and sulphuric acids as described above. Plot the readings on a graph (Fig. 5, curves A and B).

NOTE—

When dealing with a new material, should there be any fear of loss of niobium during the initial leaching with diluted hydrochloric acid (1 + 2), the following well-known procedure should be substituted as the first step.

Weigh out 1·0000 g of material into a 250-ml beaker and let it digest for a few minutes with 15 ml of concentrated hydrochloric acid. Evaporate the mixture to dryness and moisten the residue with 1 ml of diluted hydrochloric acid (1 + 1) and a little water. Warm, dilute with 50 ml of water, add 2 g of hydroxylamine hydrochloride, a little tannic acid and filter pulp, and boil for 10 minutes. Filter off the insoluble material, wash it with 2 per cent. ammonium chloride solution and ignite it in a silica or platinum crucible. Thereafter continue as described in the main procedure.

This precaution has been unnecessary with the materials dealt with so far.

MODIFICATIONS IN THE PRESENCE OF INTERFERING ELEMENTS

MODIFICATION 1: COPPER, MERCURY, PLATINUM OR MOLYBDENUM PRESENT—

Prepare a solution of antimony tribromide by dissolving 1 g of the salt in 40 ml of concentrated hydrochloric acid and diluting to 100 ml. Add an equal volume of potassium bromate solution and boil off bromine. Weigh 2·5 g of the sample, leach and ignite it as in the main procedure. Fuse it with 5 g of sodium bisulphate and extract the melt with 50 ml of 20 per cent. tartaric acid, and without filtering, transfer the extract to a 250-ml conical flask. Dilute the extract to about 75 ml, heat the solution to boiling, and add 2 ml of the antimony solution. After displacing air, pass hydrogen sulphide for 5 minutes into the closed flask under slight pressure. Filter and wash the precipitate thoroughly with hot water. Boil the filtrate, test it with hydrogen sulphide for complete precipitation, and then boil it to expel hydrogen sulphide. Add 75 ml of 20 per cent. tartaric acid, cool and make up to 250 ml. Develop and measure the colour as in the main procedure.

MODIFICATION 2: NIOBIUM PENTOXIDE CONTENT LESS THAN 0·1 PER CENT.: URANIUM, CHROMIUM, NICKEL, THORIUM, SMALL QUANTITIES OF COPPER OR LARGE QUANTITIES OF TANTALUM PRESENT—

Bring the sample into a tartaric acid solution as in the main procedure, doubling the amount of tartaric acid used for samples rich in tantalum. With a pipette, place a 10-ml aliquot in a short-stemmed stoppered 100-ml separating funnel. For samples richer in niobium take a smaller aliquot but make up to 10 ml with the tartrate - bisulphate solution of identical strength. Add 10 ml of the stannous chloride solution and 10 ml of the aqueous thiocyanate solution.

Cool the funnel under a tap for 5 minutes. Add to it 10 to 15 ml of ether, shake it for 1 minute, allow the layers to separate and run the aqueous layer into a second separating funnel. Extract it again with a similar portion of ether and separate the water layer. Pour the two ether extracts through the necks of the funnels into a 50-ml flask. Rinse the funnels with small portions of ether and add the washings to the flask. Dilute to the mark with ether, stopper the flask immediately, mix the contents and measure the optical density after 15 minutes to 2 hours, as in the main procedure. The readings should be taken as rapidly as possible, the flasks being stoppered and the glass cells covered with small glass slides.

Compare the readings with those obtained with the standard niobium solutions where 2, 4 and 6-ml aliquots of standard niobium solution are made up to 10 ml with tartaric acid - bisulphate solution. All readings are taken against a blank solution, extracted with ether in the manner described, for which 10 ml of the tartaric acid - bisulphate solution have been used.

MODIFICATION 3: TUNGSTEN PRESENT—

Make optical density measurements to determine niobium pentoxide and tungsten trioxide as described in the main procedure. With a pipette, place another 10-ml aliquot of the sample solution in a 100-ml beaker, add 10 ml of the stannous chloride solution and boil for 1 minute. Cool, transfer to a 50-ml flask and add 10 ml of the aqueous thiocyanate solution. Fill up to the mark with water and read the optical density in 4-cm cells at 436 mμ with a mercury-vapour lamp, Wratten No. 50 and Chance OB2 filters against a blank prepared in a similar manner with 10 ml of the tartrate - bisulphate solution. Find the reading on curve C of the correction graph, Fig. 5, and read the corresponding optical density on curve D. Subtract this reading from that for the total niobium and tungsten. The difference represents the optical density due to niobium.

Curves C and D of Fig. 5 are obtained as follows: prepare a standard tungsten solution by treating 0·1778 g of sodium tungstate, Na_2WO_4, in exactly the same manner as described for titanium, when 1 ml of solution contains 0·5 mg of tungsten trioxide. Use 2, 4, 6 and 8-ml aliquots to develop colour (*a*) as described in the main procedure for curve C and (*b*) as described above for tungsten correction to obtain curve D.

RESULTS

The method has been in use principally for the determination of niobium occurring as pyrochlore in the magnetite - apatite complex of Sukulu Hill, Tororo, Uganda, where about twenty minerals occur in the soil. It has, however, been tried for a number of similar soils as well as for niobium minerals themselves, as shown in Table III. The results have been compared with the gravimetric or other "exact" methods and it will be seen that the agreement has been reasonably good. In view of the fact that all gravimetric and chromatographic methods involve a colorimetric correction either for titanium or for tungsten, the accuracy of those methods cannot be greater than the accuracy of the correction itself.

TABLE III

ANALYSIS OF SOME NIOBIUM-BEARING SOILS AND MINERALS

Sample	Nb_2O_5 (thiocyanate method), %	Nb_2O_5 (gravimetric method), %	
Sukulu soil, Uganda	0·13	0·14	Analysed at the Research Division, Uganda Development Corporation Limited (U.D.C.)
	0·18	0·19	
	0·58	0·55	
	0·18	0·19	
	0·18	0·17	Average of results by several labs. communicated by Colonial Geological Surveys
	0·60	0·61	
Chilwa soil, Nyasaland	0·24	0·25	Analysed by Mineral Resources Division, Colonial Geological Surveys (gravimetric and photometric)
	0·036	0·03	
Nkumbwa soil, Northern Rhodesia	0·015	0·02	
	0·26	0·26	
	1·10	1·08	
Nigerian granite	0·15	0·16	Research Division, U.D.C.
Microlite, Kigezi, Uganda	0·83	0·93	Geological Survey of Uganda
Columbite - tantalite, Uganda	24·90	25·5	Research Division, U.D.C.
Pyrochlore concentrates from Sukulu soil, Uganda	0·41	0·43	Separated by Kipp-Kelly Ltd., Canada Analysed by Research Division, U.D.C.
	0·95	0·86	
	0·56	0·62	
	0·09	0·08	

The reproducibility of the main procedure was tested by examining the results of 32 determinations of niobium content in a large sample of Sukulu soil. The determinations were carried out in groups of eight by four different operators. A 1-g sample weighed out individually and put through the whole procedure was used for each of the 32 determinations, so that the error observed was a cumulative one comprising sampling, weighing, filtration, washing and centrifuging as well as the errors inherent in the colour development procedure. The mean value of optical density of the entire 32 samples was 0·254, corresponding to

0·18 per cent. of niobium pentoxide on total soil, with a standard deviation of 0·011 (4·4 per cent.). The standard error of the mean for 32 determinations was 0·78 per cent.

CONCLUSIONS

The work was originally undertaken with the object of providing a simple and rapid method of assaying the niobium content of the phosphatic soil deposits at Sukulu Hill in Eastern Uganda. The niobium-bearing mineral, pyrochlore, is scattered there throughout a material of highest possible complexity. Consequently, the gravimetric methods in use involved tedious separations and their standard deviation was never less than 7 per cent. It is shown above that the thiocyanate method gives not only greater speed and ease of manipulation, but also a better precision. Moreover, the need for a large number of platinum vessels for routine analyses in batches is completely eliminated. By adapting the method for use on the Hilger Spekker absorptiometer, an expensive spectrophotometer, which is only of limited use in routine analytical laboratories, is unnecessary. The extension of the method to other low-grade niobium ores has presented no difficulties. Also minerals rich in niobium or tantalum minerals with small niobium content have been analysed successfully. So far, no niobium minerals containing metals causing the most serious interference, *i.e.*, uranium, vanadium, molybdenum and tungsten, have been available. Small amounts of uranium and tungsten present in some minerals were insufficient to require the use of the special modifications described. Those have been tried out on synthetic materials only. The method appears to afford the best means of assessing the ratio of niobium to tantalum in the mixed oxides precipitated from columbite, tantalite and similar ores rich in both elements.

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RESEARCH DIVISION
ENTEBBE, UGANDA

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Inorganic Chromatography on Cellulose

Part XIV

A Shortened Chromatographic Method for the Determination of Niobium and Tantalum in Minerals and Ores

By R. A. MERCER and R. A. WELLS

(*Presented at the meeting of the Society on Wednesday, November 4th,* 1953)

A chromatographic procedure is described for the extraction of the mixed oxides of tantalum and niobium from minerals and ores. A solution of the sample in hydrofluoric acid containing ammonium fluoride is absorbed on cellulose and transferred to a 3-inch column of cellulose. The niobium and tantalum are completely extracted on passing 400 ml of ethyl methyl ketone containing 15 per cent. v/v of 40 per cent. w/v hydrofluoric acid through the column. The separation is complete from all metals other than tungsten. The two oxides, recovered from this solvent, are subsequently separated by further chromatography or determined without separation by a suitable colorimetric procedure.

DURING the routine analysis of a wide variety of natural minerals and synthetic concentrates, need has arisen for a rapid method for the determination of tantalum and niobium that incorporates a quick and efficient method of sample breakdown. Published methods[1] for the chemical separation of tantalum and niobium from other metals tend to be rather lengthy and are not generally applicable to all materials. Previous workers have shown the possibility of separating tantalum and niobium oxides from other metals by a chromatographic method[2] and in later work[3,4,5] this technique was applied to the separation of tantalum from niobium. These methods, although accurate, are time-consuming. This paper describes a chromatographic method for the separation of niobium and tantalum based upon the previously described methods, but affording some saving in time and chemicals.

The previous chromatographic methods involved the extraction of a fluoride solution of the sample on a cellulose column with ethyl methyl ketone. The tantalum was first extracted with ethyl methyl ketone saturated with water. The column was then washed through with ethyl methyl ketone containing 1 per cent. v/v of hydrofluoric acid (40 per cent. w/v) to lower its water content. Finally, the niobium was extracted with ethyl methyl ketone containing 12·5 per cent. of hydrofluoric acid (40 per cent. w/v). The total volume of solvent used was large, being about 1200 ml. In the present method the length of the cellulose column has been shortened from 12 to 3 inches and the acid content of the solvent has been increased to 15 per cent. v/v of hydrofluoric acid (40 per cent. w/v). Under these conditions 400 ml of solvent have been found to extract tantalum and niobium together quantitatively. Often the concentration of mixed oxides is all that is required, but when the individual concentrations are required, the mixed oxides can be treated in one of two ways. They can be submitted to a further chromatographic separation in which the tantalum is extracted, free from niobium, with ethyl methyl ketone saturated with water or, more speedily, the tantalum and, if required, the niobium, can be determined colorimetrically.[7] A suitable colorimetric procedure for the determination of each of the two metals is given in the following paper[6] (see p. 345). The modified method has the further advantage that up to 800 mg of mixed oxides can be extracted with 400 ml of solvent, as compared with less than 100 mg extracted by the same volume of solvent containing 7·5 per cent. v/v of hydrofluoric acid used in earlier experiments.

With the exception of samples that were completely soluble in a mixture of hydrofluoric and nitric acids, a fusion with potassium bisulphate has been used to break down the sample. For low-grade materials this is inconvenient because of the large weight of sample that has to be treated. If it is desired to apply the method to such materials, an acid attack followed by concentration of a niobium-bearing fraction by acid hydrolysis may be used. This type of pre-treatment was used by Williams and Mercer in earlier work.[4] For low-grade materials, however, a paper-strip chromatographic method described in a later paper[7] (see p. 351) is now preferred for the determination of niobium. For higher-grade materials (containing more than 1·0 per cent. of niobium pentoxide) the sample is fused with potassium bisulphate. The melt is extracted with dilute sulphuric acid and the boiling extract is made alkaline with ammonium hydroxide. The precipitated hydroxides are filtered and gently ignited. The ignited residue is dissolved in hydrofluoric acid and, after addition of 1 g of ammonium fluoride, is transferred to the chromatographic column. Under these conditions, for samples high in titanium, the total weight of oxides transferred to the column must not exceed 1 g if the risk of partial extraction of titanium is to be avoided. The effect of larger quantities of ammonium fluoride has not yet been investigated. In spite of the limitations placed on the weight of oxides transferred to the cellulose column, more than 1 g of original sample can often be taken for the bisulphate fusion, as some elements will be lost in the subsequent ammonium hydroxide precipitation. For samples containing little or no titanium, the weight taken can be increased to several grams.

The final fluoride solution of the sample is prepared in 6 ml of 25 per cent. hydrofluoric acid (25 ml of 40 per cent. w/v hydrofluoric acid and 75 ml of water). Details for the transfer of the solution to the column are described under the method given later, together with the packing of the column and the preparation of the solvent. The 400 ml of solvent used in the extraction are evaporated and the residue is washed into a platinum dish. The residue is heated to fumes with sulphuric acid to remove fluoride and, after dilution with water, the acid solution is made alkaline with ammonium hydroxide. The precipitated acidic oxides are filtered off, ignited and weighed. The alkaline precipitations before and after extraction remove molybdenum, potassium, phosphate and vanadium, all of which are partly extracted from the cellulose column. Any potassium and sulphate remaining after the first hydroxide precipitation did not affect the extraction of niobium and tantalum. Phosphoric acid passed readily through the column and for minerals high in phosphate it was found desirable to repeat the second precipitation with ammonium hydroxide. Spectrographic examination of the final mixed oxides of tantalum and niobium showed that they possessed a high degree of purity (see Table I). The only serious contaminant was tungsten. A small portion of that present in the original sample was extracted with the niobium and tantalum and was not extracted during the ammonium hydroxide precipitation. The proportion of tungsten extracted was illustrated by an experiment in which 0·5 g of tungsten trioxide was mixed with 0·3 g of niobium pentoxide and the two were extracted in a column; 0·005 g of tungsten trioxide was extracted with the niobium. The weight of extracted oxides was corrected for tungsten after determination of tungsten by the colorimetric method described later.

Some experiments were carried out in which a precipitation with tannic acid at pH 4 to 5 replaced the final ammonium hydroxide precipitation; but the alkaline precipitation was found to give the better separation from potassium and phosphate ions.

TABLE I

THE PURITY OF EXTRACTED OXIDES AS DETERMINED BY SPECTROGRAPHIC ANALYSIS

Sample number	Fe, %	Mo, %	Sn, %	Ti, %	Zr, %
8a	0·1 to 0·3	<0·1	0·03 to 0·10	<0·01	<0·1
3a	0·03 to 0·1	<0·1	0·03 to 0·10	<0·01	<0·1
5b	0·03 to 0·1	—	<0·01	<0·01	<0·1

TABLE II

EXTRACTION OF THE OXIDES OF NIOBIUM AND TANTALUM FROM SYNTHETIC MIXTURES

Column length, inches	40% HF in solvent, % v/v	Weight of oxides taken			Total Ta_2O_5+ Nb_2O_5 added, mg	Weight of mixed oxides recovered in each 100-ml fraction of solvent, mg							Total weight of Ta_2O_5+ Nb_2O_5 recovered, mg	Ta_2O_5+ Nb_2O_5 recovered, %
		Ta_2O_5, mg	Nb_2O_5, mg	TiO_2, mg		1	2	3	4	5	6	7		
6	7·5	10·0	80·0	50	90·0	7·4	8·6	21·2	26·0	15·1	11·2	0·8	90·3	100·4
6	12·5	8·4	79·9	50	88·3	←		88·0		→	0·7	0·3	89·0	100·8
3	12·5	10·0	91·2	50	101·2	←		100·5	→	1·0	0·2	0	101·7	100·5
6	15·0	8·0	80·4	50	88·4	9·5	63·5	13·3	2·0	—	—	—	88·2	99·8
3	15·0	9·2	71·5	50	80·7	13·2	63·0	4·3	0	←	0	→	80·5	99·8
3	20·0	6·5	73·7	50	80·2	72·9	7·0*	2·8*	11·9*	*	*	*	—	—
3	15·0	8·5	76·9	50	85·4	← 56·4	→	← 28·9	→	←	0·1	→	85·3	99·9
3	15·0	60·9	8·0	50	68·9	58·6	9·3	0·5	0·8	←	0	→	69·2	100·4
3	15·0	6·0	74·7	50	80·7	10·1	39·8	21·1	9·3	←	0	→	80·3	99·5
3	15·0	140·5	70·0	50	210·5	←	210·3	→	←		0	→	210·3	99·9
3	15·0	263·8	121·2	125†	385·0	←	385·8		→	0·3	—	—	385·8	100·2
3	15·0	99·7	260·5	125†	360·2	←	359·6		→	0·2	—	—	359·6	99·8
		Ta_2O_5	Nb_2O_5	WO_3										
3	15·0	nil	268·7	520	268·7	←	274·4 WO_3 colorimetrically 6·0 mg		→	—	—	—	268·4	99·9
3	15·0	nil	796·3	465 + 0·93 g of $(NH_4)_2HPO_4$	796·3	←	805·3 WO_3 colorimetrically 12·1 mg		→	—	—	—	793·2	99·6

* Titanium present in oxide. All oxides were free from titanium unless otherwise indicated.

† 1 g of a mixture containing equal parts of Fe_2O_3, Al_2O_3, ThO_2, TiO_2, ZrO_2, SnO_2, rare-earth oxides and a niobium-free granite was added to the pure oxide sample.

EXPERIMENTAL

A series of experiments was carried out to determine the optimum conditions of column length and solvent acidity for complete and rapid extraction of niobium and tantalum oxides. Mixtures of pure tantalum and niobium metals were weighed out and dissolved in hydrofluoric acid. About 50 mg of titanium dioxide were added to provide a guide to the possible extraction of impurities. These mixtures were extracted in columns of cellulose of various lengths, packed in 2-cm diameter polythene tubes, with ethyl methyl ketone containing various concentrations of 40 per cent. w/v hydrofluoric acid. The results, shown in Table II, indicated that the extraction of niobium and tantalum from a 3-inch column was complete with 400 ml of ethyl methyl ketone containing 15 per cent. of 40 per cent. w/v hydrofluoric acid solution. Increasing the column length to 6 inches increased the volume of solvent required to 500 ml. The rate of extraction of the two metals increased with increase of acid concentration in the solvent, but at 20 per cent. of 40 per cent. w/v hydrofluoric acid in the solvent, titanium was also extracted. With the 15 per cent. hydrofluoric acid solvent mixture, extraction was complete in 400 ml of solvent irrespective of whether niobium or tantalum was in excess. Having attained satisfactory extraction from titanium with a 3-inch column and the 15 per cent. hydrofluoric acid solvent mixture, two further experiments were carried out under the same conditions but with the addition of 1 g of a mixture of equal parts of Fe_2O_3, Al_2O_3, ThO_2, TiO_2, ZrO_2, SnO_2, rare-earth oxides and a granite, to known weights of niobium and tantalum. In the first experiment tantalum was added in excess of niobium and in the second the ratio of the two was reversed. In both, the separation and recovery was satisfactory. Two further experiments were carried out on mixtures of niobium and tungsten oxides. In the first, about 1 per cent. of the tungsten was extracted with the niobium and was subsequently determined colorimetrically in the niobium pentoxide. In the second, ammonium phosphate was added, in addition to the tungsten, in order to ascertain whether phosphate increased the extraction of tungsten. Some increase in tungsten extracted was observed, but it is doubtful whether the increase was sufficiently large to be attributed to phosphate. In this last experiment the niobium pentoxide extracted amounted to almost 0·8 g and the recovery was virtually complete.

METHOD

REAGENTS—

Potassium bisulphate—Finely ground powder.

Sulphuric acid—A 5 per cent. v/v solution.

Ammonium hydroxide, sp.gr. 0·880.

Ammonium nitrate - ammonium hydroxide solution—Dissolve 5 g of ammonium nitrate in 100 ml of water and add 2 ml of ammonium hydroxide, sp.gr. 0·880.

Hydrofluoric acid—A 40 per cent. w/v solution.

Nitric acid, sp.gr. 1·42.

Ammonium fluoride.

Cellulose powder—Whatman's standard grade.

Ethyl methyl ketone - hydrofluoric acid solvent—Purify the commercial ketone in bulk by heating 5 gallons of it with a mixture of 60 g of potassium permanganate and 100 g of sodium bicarbonate in 3 litres of water for 2 hours under a reflux condenser. Separate the ketone layer and dry it, first over calcium chloride, then over caustic soda. Re-distil the dried product.

To prepare the solvent mixture add 15 ml of 40 per cent. w/v hydrofluoric acid to 85 ml of pure ethyl methyl ketone, with the aid of a polythene measuring cylinder. Store it in a polythene bottle.

Sulphuric acid, sp.gr. 1·84.

PROCEDURE—

Weigh sufficient finely ground sample to provide a convenient final weight of oxides and fuse it carefully with a 10 to 15 times excess of potassium bisulphate in a platinum or silica crucible until the melt is clear. The potassium bisulphate should preferably be fused to a dull-red heat before addition of the sample. This removes any water present and results in a fusion with less spitting. Leach the sample out of the crucible with 200 ml of 5 per cent. sulphuric acid. Boil the solution until the melt is completely broken up. Precipitate the hydroxides from the boiling solution by addition of an excess of ammonium hydroxide solution. Separate the precipitate by filtration and wash it with a wash solution containing 2 per cent. of ammonium hydroxide solution and 5 per cent. of ammonium nitrate. Ignite the hydroxides and the filter-paper very gently at 500° to 600° C in a platinum dish. Avoid excessive heating. Digest the ignited oxides with a hydrofluoric - nitric acid mixture and remove the nitric acid by repeated evaporations with hydrofluoric acid. While the solution is evaporating, prepare a cellulose column by the method described in the note below. To the dried fluorides add 1 g of ammonium fluoride, 4·5 ml of water and 1·5 ml of 40 per cent. w/v hydrofluoric acid. Warm the mixture gently for a few minutes to effect solution of the sample, but avoid evaporation of the acid. Allow the mixture to cool, add 5 g of cellulose powder and stir well to get an intimate mixture. An almost dry mixture of powder and sample should result. Transfer the contents of the dish to the cellulose column previously prepared. Beat up the sample wad with a polythene plunger until no lumps remain. Rinse the plunger with the solvent and then remove it. Remove the stopper from the foot of the column and allow the solvent level in the column to fall to the level of the wad. Collect the eluate in a 600-ml polythene beaker. Do not allow the column to become dry. Elute the column with a total of 400 ml of solvent. Make each small addition of the solvent via the platinum dish in order to ensure complete removal of the sample. Evaporate the solvent by fully immersing the beaker in a steam-bath and directing a jet of air on the surface of the solvent. Transfer the residue from the beaker to a tared platinum dish and evaporate it almost to dryness under an infra-red lamp. Add 5 ml of concentrated sulphuric acid plus a few drops of nitric acid and evaporate the mixture to fumes of sulphur trioxide. Wash the contents of the dish into a 400-ml beaker, dilute to 250 ml, heat to boiling, add ammonium hydroxide solution until neutral, and then add 10 ml of ammonium hydroxide, sp.gr. 0·880. Digest the precipitate for half an hour. Filter and wash the precipitate with a hot solution containing 5 per cent. of ammonium nitrate and 2 per cent. of ammonium hydroxide solution. Ignite the precipitate to a mixture of niobium and tantalum pentoxides in a tared dish. If the sample is highly phosphatic, the ignited oxides should be redissolved in hydrofluoric acid, heated to fumes with sulphuric acid and the ammonium hydroxide precipitation repeated. Determine the tantalum and/or niobium in the mixed oxides by a colorimetric method[6] as described on p. 345. Determine the tungsten in the mixed oxides by the colorimetric procedure described below.

NOTE—

Preparation of the cellulose column—Close the end of a polythene chromatographic tube with a small rubber bung. The tube should be 12 inches long and of $\frac{3}{4}$ inch internal diameter. The bottom end should be tapered so that it narrows down to $\frac{1}{4}$ inch internal diameter. Addition of the sample is easier if the top end of the tube is flanged. Fill the tube to a depth of 9 inches with a solvent consisting of ethyl methyl ketone containing 15 per cent. v/v of hydrofluoric acid (40 per cent. w/w aqueous solution). Add cellulose powder judged to be sufficient for a 3-inch column and, with a polythene plunger, beat up the slurry produced, taking care to remove all air bubbles. Remove the plunger and allow the column of solid to settle under its own weight. Let the column drain until the solvent level is within 3 inches of the top of the cellulose and stop the flow. The column is now ready for use.

THE ABSORPTIOMETRIC DETERMINATION OF TUNGSTEN IN A MIXTURE OF NIOBIUM AND TANTALUM OXIDES

REAGENTS—

Sodium carbonate—Pure anhydrous solid.

Potassium thiocyanate—A 25 per cent. w/v solution in water.

Stannous chloride—Dissolve 10 g of stannous chloride, $SnCl_2.2H_2O$, in 90 ml of hydrochloric acid, sp.gr. 1·18.

Sodium tungstate—A solution containing the equivalent of 0·2 mg of tungsten trioxide per ml.

Sodium carbonate solution, 0·5 N.

PROCEDURE—

The method used closely follows that described by Schoeller[1] except that the colour intensity is measured with a spectrophotometer. Fuse about 50 mg of oxides with 1·3 g of sodium carbonate in a platinum crucible. Dissolve the melt in warm water; transfer the solution to a 50-ml calibrated flask and dilute it to the mark. Filter this solution and, with a pipette, place a 20-ml aliquot of the filtrate in a 50-ml calibrated flask. Add 2·5 ml of 25 per cent. potassium thiocyanate solution and make up to volume with a solution of 10 g of stannous chloride in 90 ml of concentrated hydrochloric acid. Allow the colour to develop for 30 minutes and measure the transmission at 420 mμ against a water blank. Determine the tungsten content by reference to a standard curve prepared from sodium tungstate solution containing 0·2 mg of tungsten per ml diluted to 20 ml with 0·5 *N* sodium carbonate solution and treated in the same manner as the sample.

TABLE III

DETERMINATION OF $(Ta,Nb)_2O_5$ IN ORE SAMPLES

Sample	Wt. of sample taken, g	Wt. of oxides added, g		$(Ta,Nb)_2O_5$ found, %	Mean $(Ta,Nb)_2O_5$ found, %	WO_3 in mixed oxides, %
		Ta_2O_5	Nb_2O_5			
1. Pyrochlore concentrate *a*	3·0662			2·00	2·00	—
b	3·0028			2·00		0·20
2. Pyrochlore concentrate *a*	2·0074			7·25	7·27	0·28
b	3·0442			7·23		—
c	3·2226			7·34		—
3. Ilmeno-rutile *a*	2·0051			31·41	31·28	0·46
b	0·8413			31·19		—
c	0·9595			31·24		—
4. Chemical concentrate from pyrochlore *a*	0·5128			64·74	64·63	0·08
b	0·4983			64·52		—
c	0·5724			64·63		—
5. Chemical concentrate from pyrochlore *a*	0·3139			76·17	76·25	—
b	0·3036			76·22		0·59
c	0·3247			76·35		—
6. Ilmeno-rutile *a*	0·9996			3·23	3·40	—
b	1·0012			3·39		2·30
c	1·0018			3·46		—
d	2·0005			3·54		—
e	1·0348	0·0331	0·0365	3·34	3·34	—
7. Ilmeno-rutile *a*	1·0002			3·50	3·58	—
b	2·0050			3·63		1·30
c	1·7278			3·62		—
d	2·1737	0·0362	0·0650	3·57	3·57	—
8. Ilmeno-rutile *a*	2·0005			21·50	21·46	1·70
b	1·0348			21·28		—
c	1·2108			21·59		—
d	0·9111	0·0546	0·0587	21·39	21·46	—
9. Pyrochlore concentrate *a*	0·3736			45·40	45·42	0·49
b	0·3563			45·44		—
c	0·3072	0·0255	0·0741	45·25	45·25	—

RESULTS

The method has been applied to the determination of niobium and tantalum in a number of samples of physical and chemical concentrates of pyrochlore and ilmeno-rutile. Results found (Table III) showed excellent repeatability. The quantitative character of the extraction was determined by adding niobium and tantalum to analysed samples and repeating the determination. After allowing for added oxides in the final weight of extracted mixed oxides, results were in good agreement with the original determinations. The ilmeno-rutile samples were as mined, having undergone no beneficiation. The pyrochlore concentrates included samples obtained by mineral dressing of low-grade material and chemical concentrates produced from these dressed materials.

The authors wish to thank Mr. J. R. Moore who carried out the spectrographic determinations and Mrs. P. Macdonald for experimental assistance.

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CHEMICAL RESEARCH LABORATORY
TEDDINGTON, MIDDLESEX

January 29th, 1954

The Absorptiometric Determination of Niobium and Tantalum with Pyrogallol

BY E. C. HUNT AND R. A. WELLS

(*Presented at the meeting of the Society on Wednesday, November 4th*, 1953)

Absorptiometric procedures are described for the determination of niobium and tantalum in mixtures of their oxides. The method is applied to the determination of the two metals in mixtures obtained by their chromatographic extraction from minerals and ores. The determinations depend on the formation of a coloured complex between tantalum and pyrogallol in acid solution and between niobium and pyrogallol in alkaline solution. Both systems obey Beer's law, and, with 1-cm cells, the optimum limits of concentration are 0 to 20 p.p.m. for niobium and 0 to 80 p.p.m. for tantalum. The effect of variation in pH and the interference of a number of cations and anions are recorded.

SEVERAL chromatographic procedures for the separation of niobium and tantalum from minerals and ores have been described in earlier reports.[1,2,3,4,5] At present the most favoured method[5] is to separate niobium and tantalum together from other constituents of the sample and then to carry out a further chromatographic separation of the mixture of the two metals. The second separation is time-consuming and, moreover, when either of the two metals present is in a small proportion, it can give too small a weight of the recovered metal oxide for an accurate result by weighing. This difficulty has been overcome by determining the tantalum absorptiometrically in the mixed oxides. The niobium content can then be calculated by difference and, if desired, can be checked by direct colorimetric determination on the mixed oxides.

The colorimetric procedure for both metals is carried out on an oxalate solution of the mixed oxides. The solution is prepared by fusing the pure mixed oxides, derived chromatographically or by other means, with potassium bisulphate and leaching the melt with ammonium oxalate solution. Tantalum is determined by adding an acid solution of pyrogallol to an aliquot of the oxalate solution and determining the optical density of the yellow colour produced, with the aid of a spectrophotometer with light of wavelength 400 mμ. Niobium is determined by adding an alkaline solution of pyrogallol to an aliquot of the oxalate solution of the metals and measuring the density of the yellow colour produced, this time with light of wavelength 410 mμ.

Unlike previous workers,[6] we have found that niobium interferes with the tantalum determination and tantalum interferes with the niobium determination, but in both determinations the interference is linear and a correction can be made. Both pH and salt concentration markedly affect the colours and must be strictly controlled. Under suitable conditions 0 to 2 mg of tantalum pentoxide or 0 to 25 mg of niobium pentoxide can be determined with an accuracy of 5 per cent.

FACTORS INFLUENCING THE COLOUR GIVEN BY TANTALUM—

In earlier work by Platonov and Krivoshlikov[6] on the tantalum - pyrogallol colour reaction, with a visual comparison type of colorimeter, it is recorded that niobium does not interfere under acid conditions. Milner and Wood[7] used a Spekker absorptiometer and found that colour complexes were not formed, under specified conditions, between pyrogallol and solutions containing uranium, niobium or iron. Their method has formed the basis of the colorimetric tantalum procedure described in this paper.

Measurements for the colorimetric determination of both niobium and tantalum were made with a Unicam spectrophotometer. Early experiments indicated that the tantalum - pyrogallol colour was affected by the potassium bisulphate, ammonium oxalate and pyrogallol concentrations. The results were reproducible when the colour was developed in a solution containing 4 per cent. of ammonium oxalate, 2 per cent. of potassium bisulphate, 1·6 per cent. of pyrogallol and 0·2 per cent. of concentrated sulphuric acid. These conditions allow the use of sufficient bisulphate to dissolve the mixed oxides on fusion, while keeping the concentration too low for the formation of a precipitate of potassium tetroxalate. The final solution had a pH of 1 to 2. The effect on the colour of variation of pH by addition of sulphuric acid or ammonium hydroxide is recorded in Table I. All density readings were taken against a reagent blank prepared at pH 3·5, and at a wavelength of 400 mμ. Readings found for niobium, for various values of pH, under the same conditions used for tantalum, are also recorded in Table I. The results show that, for both metals, the variation of optical density with pH decreases as the acidity of the solution increases. At the same time the difference in the intensities of the colours produced by the two metals increases and favours the tantalum determination. The use of a wavelength of 400 mμ was based on an examination of the absorption spectra curves, Fig. 1. At this wavelength, there is a high absorption for a tantalum solution with a small but positive absorption for a niobium solution.

TABLE I

EFFECT OF pH ON NIOBIUM - PYROGALLOL AND TANTALUM - PYROGALLOL COLOURS

pH	Density reading for 0·80 mg of Ta_2O_5	Density reading for 5·0 mg of Nb_2O_5
2	0·341	0·084
3	—	0·092
4	0·330	0·369
5	—	0·800
5·5	0·283	—

the intensities of the colours produced by the two metals increases and favours the tantalum determination. The use of a wavelength of 400 mμ was based on an examination of the absorption spectra curves, Fig. 1. At this wavelength, there is a high absorption for a tantalum solution with a small but positive absorption for a niobium solution.

The interference of a number of anions was briefly investigated (see Table II) and the interference of a number of cations is shown in the first column of Table III (p. 348).

TABLE II

THE EFFECT OF ANIONS ON THE COLOUR OF TANTALUM PENTOXIDE

0·80 mg of Ta_2O_5 taken	
Substance added	Ta_2O_5 found, mg
1% of H_2SO_4	0·79
1% of H_2SO_4 + 2% of K_2SO_4	0·86
1% of H_3PO_4	0·78
4% of NH_4F	nil

METHOD

REAGENTS—

Potassium bisulphate solution—Fuse 10 g of potassium bisulphate under the same conditions as those used for the solution of the mixed oxides. Dissolve the melt in water and dilute to 100 ml. Then 1 ml of solution contains 0·1 g of potassium bisulphate.

Acid pyrogallol solution—Dissolve 10 g of resublimed pyrogallol in a solution of 2·5 ml of diluted sulphuric acid (1 + 1, v/v) and 35 ml of water. Filter this solution through a Whatman No. 42 filter-paper into a 50-ml calibrated flask. Wash the paper with water and dilute to the mark on the flask. This solution is stable for several days.

Ammonium oxalate solution, 4 per cent.—Dissolve 4 g of ammonium oxalate in 100 ml of water.

PROCEDURE—

Place 0·5 g of fused potassium bisulphate in a small platinum or silica crucible and heat it gently until spitting ceases. Allow the crucible to cool. Weigh accurately about 25 mg of the finely ground mixed oxides and transfer them to the bisulphate melt with the aid of a camel-hair brush. Hold the crucible over a low flame and swirl the contents continuously until the oxides have dissolved. If the oxides are not readily soluble, allow the bisulphate to cool, add 3 drops of sulphuric acid and repeat the fusion. Allow the melt to cool; then add 1 g of ammonium oxalate and 10 ml of water. Warm the crucible on a hot-plate until the solution is clear. Allow the solution to cool to 30° to 40° C (potassium and ammonium oxalates may crystallise at this stage if the solution cools too much) and transfer it to a 25-ml calibrated flask. Cool the flask and its contents to 20° C and dilute to the mark. With a pipette, place 5 ml of this solution in a 25-ml calibrated flask and add 4 ml of potassium bisulphate solution (0·1 g per ml) and 0·8 g of finely ground ammonium oxalate. If required, 10 ml of sample solution can be used; then 3 ml of potassium bisulphate solution and 0·6 g of ammonium oxalate are added. Dilute to 20 ml and shake to obtain complete solution. Add 2 ml of acid pyrogallol solution with a pipette and dilute to the mark. Read the transmission of the solution against a reagent blank for light of wavelength 400 mμ with a quartz-prism spectrophotometer. Calculate the niobium interference and subtract this value from the tantalum figure. The blank may be prepared by placing, with a pipette, 5 ml of potassium bisulphate solution in a 25-ml flask and then adding 1·0 g of ammonium oxalate and 2 ml of pyrogallol solution, as for the sample.

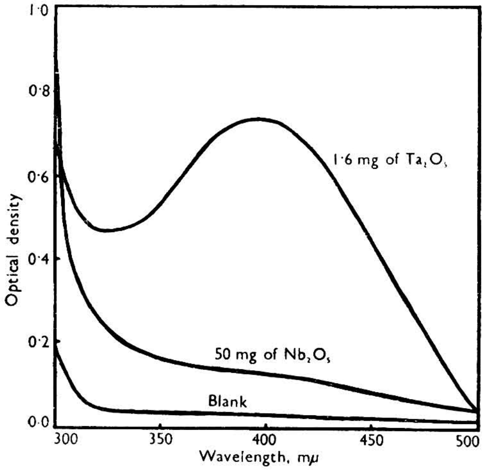

Fig. 1. Absorption curves for tantalum and niobium in acid pyrogallol

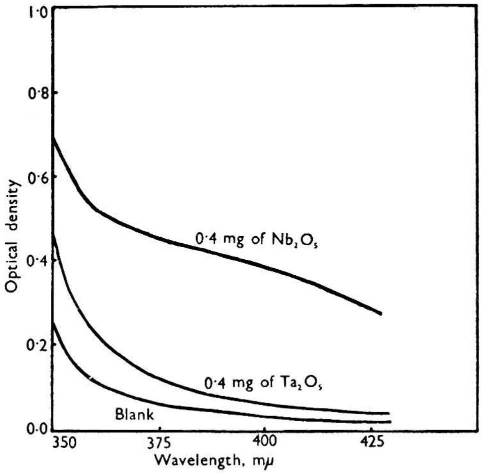

Fig. 2. Absorption curves for tantalum and niobium in alkaline pyrogallol

FACTORS INFLUENCING THE COLOUR GIVEN BY NIOBIUM—

Platonov and Krivoshlikov[6] determined tantalum or niobium under the appropriate conditions of acid or alkaline medium and then eliminated the first colour and developed the colour of the other element by addition of sodium sulphite or sulphuric acid. We have found, however, that the addition of dilute sulphuric acid to a solution containing ammonium oxalate, sodium sulphite and pyrogallol produces a yellow colour, even in the absence of tantalum and niobium. Therefore, we preferred to carry out the niobium determination on a fresh aliquot of sample solution. The colour produced by niobium with pyrogallol in sodium sulphite solution is sensitive to pH. It increases with increasing pH and with very high pH conditions the colour alters from yellow toward green. The amounts of reagents used in the procedure adopted in this paper give a solution of pH 7 to 8. In this range the variation of optical density of the niobium solution with pH is small. Rigid adherence to the specified conditions is necessary in order to ensure reproducible results.

The optical density measurements were made at 410 mμ. An examination of the absorption curves (Fig. 2) indicated that at this wavelength a reasonable sensitivity for niobium could be attained with only a little interference from tantalum. The interference caused by the presence of a number of other cations is shown in the second column of Table III.

TABLE III

INTERFERENCE OF CATIONS ON NIOBIUM AND TANTALUM DETERMINATIONS

Tantalum determination in acid medium		Niobium determination in alkaline medium	
1 mg of metal oxide	Ta_2O_5 equivalent, mg	1 mg of metal oxide	Nb_2O_5 equivalent, mg
Fe_2O_3	0·19	Fe_2O_3	Intense violet colour
WO_3	0·20	WO_3	0·11
MoO_3	0·68	MoO_3	0·84
ZrO_2	0·00	ZrO_2	0·02
TiO_2	4·00	TiO_2	3·10
V_2O_5	0·44	V_2O_5	Deep blue colour
SnO_2	0·00	SnO_2	<0·01
Nb_2O_5	0·0072	Ta_2O_5	0·03

METHOD FOR THE DETERMINATION OF TANTALUM

REAGENTS—

Sodium sulphite solution, 20 per cent.—Dissolve 20 g of analytical-reagent quality sodium sulphite, $Na_2SO_3.7H_2O$, in water and dilute to 100 ml. Prepare this solution just before use.

Alkaline pyrogallol solution—Dissolve 1 g of resublimed pyrogallol in 30 ml of 20 per cent. sodium sulphite solution and filter this solution through a Whatman No. 42 filter-paper into a calibrated flask. Wash the paper with sufficient sodium sulphite solution to bring the volume to 50 ml. This solution must be prepared immediately before use as it may become discoloured after a few hours.

PROCEDURE—

For the determination of tantalum the sample was fused with bisulphate and the melt was dissolved in 25 ml of ammonium oxalate solution. For the determination of niobium place, with a pipette, 1 ml of the oxalate solution prepared for the tantalum determination in a 50-ml calibrated flask. Add to it 5 ml of potassium bisulphate solution (0·1 g per ml), 20 ml of 4 per cent. ammonium oxalate solution and 20 ml of alkaline pyrogallol solution. Dilute the solution to 50 ml. Take a reading of the transmission of the solution for light of wavelength 410 mμ against a blank on the reagents, with a quartz-prism spectrophotometer. Calculate the interference due to tantalum and subtract it from the niobium value.

It was found essential to prepare the sodium sulphite solution, used in preparing the pyrogallol solution, immediately before use. The pyrogallol solution was also prepared fresh. Use of sodium sulphite solution that had been standing for some time in a glass-stoppered bottle led to too low a pH in the final coloured solution, resulting in low niobium results. Use of a large excess of sodium sulphite solution was found necessary to ensure that the pH of the measured solution should be close to 8.

PREPARATION OF STANDARD CURVES—

Standard curves were prepared by weighing pure tantalum and niobium oxides and preparing oxalate solutions from them as already described for mixed oxides. Aliquots of these solutions were taken for colorimetric determination.

The tantalum curve was plotted over the range 0 to 2 mg of tantalum pentoxide (0 to 80 p.p.m.), see Fig. 3. The correction curve for niobium was plotted on the same graph over the range 0 to 25 mg of niobium pentoxide (0 to 1000 p.p.m.). To find the tantalum concentration in a sample, the apparent tantalum concentration was read and the figure was subtracted from the known weight of mixed oxides present to give an approximate niobium pentoxide concentration. The transmission reading for which this amount of niobium would be responsible was read from the niobium correction curve. The weight of tantalum pentoxide equivalent to this transmission was subtracted from the original apparent figure for tantalum pentoxide to give the "true" figure for tantalum pentoxide. The correction process may be repeated, but the effect upon the result is negligible.

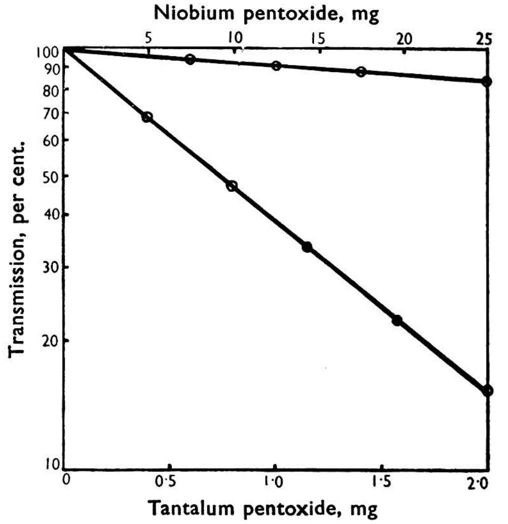

Fig. 3. Standard curve for tantalum

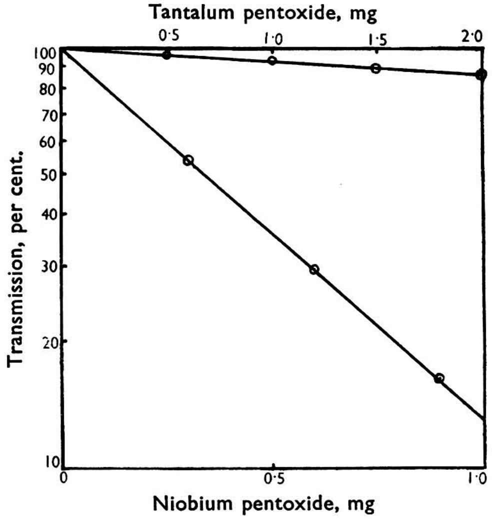

Fig. 4. Standard curve for niobium

The standard niobium curve was plotted over the range 0 to 1 mg of niobium pentoxide (0 to 20 p.p.m.), see Fig. 4. The correction curve for tantalum was plotted on the same graph and was used to find a true figure for niobium in a similar manner to that described for tantalum in the preceding paragraph.

RESULTS

The methods have been applied to the determination of tantalum and niobium in a number of mixed oxides obtained chromatographically from minerals mainly of the ilmenorutile and pyrochlore type. In Table IV the results from chromatography are compared with those found by gravimetric analysis after further chromatographic separation of the mixed oxides. Although the chromatographic procedure does result in mixed oxides free from iron, titanium and a number of other interfering elements, tungsten is present as an impurity, if present in the original sample. When tungsten was present in the mixed oxides it was determined colorimetrically, and a correction was made in calculating the results in Table IV.

The figures shown in Table IV result from two determinations of the mixed tantalum and niobium oxides on each sample. One sample of mixed oxides was used for the colorimetric determination of tantalum, niobium and tungsten, and the percentage of mixed oxides in the original sample, recorded in the second column, is based upon this first determination. The mixed oxides from the second chromatographic separation were again separated by chromatography to get the gravimetric tantalum figure recorded in the fourth column. The gravimetric niobium figure was found by subtracting the gravimetric tantalum figure from the mixed oxide percentage shown in the second column.

Assuming the gravimetric results to be correct, the niobium and tantalum colorimetric results, with two exceptions amongst the tantalum figures, are accurate to 5 per cent.

TABLE IV

DETERMINATIONS OF TANTALUM AND NIOBIUM IN ORES

Sample	$(Nb,Ta)_2O_5$, %	Ta_2O_5, %		Nb_2O_5, %	
		Colorimetric	Gravimetric	Colorimetric	Gravimetric
Pyrochlore concentrate	2·00	0·23	—	1·69	—
	64·78	6·04	6·11	58·58	58·69
	14·98	0·96	0·99	13·93	13·99
Ilmeno-rutile	31·27	11·07	10·93	20·48	20·34
	3·46	0·98	0·88	2·49	2·58
	21·27	4·93	5·02	16·19	16·25
	3·31	0·69	—	2·55	—
	20·92	5·65	5·55	14·83	15·37
	15·18	3·71	3·70	11·42	11·48
Pyrochlore concentrate	62·64	5·13	5·02	57·75	57·62
	9·16	0·46	0·48	8·74	8·68
	2·00	0·22	—	1·63	—
	64·69	5·77	5·78	58·26	58·91
	29·66	2·08	2·07	27·40	27·59
	24·36	1·58	1·55	22·77	22·81
	7·23	0·49	0·44	6·93	6·79
	56·23	6·10	6·07	—	50·16
	43·80	3·57	3·62	—	40·18

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January 29*th*, 1954

Inorganic Chromatography on Cellulose

Part XV

A Rapid Chromatographic Method for the Determination of Niobium in Low-grade Samples

By E. C. HUNT and R. A. WELLS

(*Presented at the meeting of the Society on Wednesday, November 4th, 1953*)

A rapid and simple chromatographic method is described for the determination of niobium in a hydrofluoric acid solution of an ore by upward diffusion on a paper strip. The niobium is detected as a yellow band on spraying the strip with aqueous tannic acid. An accurate determination of niobium is made by direct visual comparison of the band with standard strips. The chromatographic separation takes 20 minutes, and a simple technique is described for carrying out ten separations simultaneously. The accuracy is 10 per cent. on ores containing more than 0·10 per cent. of niobium pentoxide.

THE present growing interest in niobium has resulted in an urgent demand, particularly by mineral-dressing and plant control laboratories, for a quick method for the determination of this element. A number of colorimetric,[1,2,3,4,5,6,7] titration[8] and spectrographic procedures have been described; these, although sufficiently accurate, are somewhat lengthy, owing to the need for a preliminary separation of the niobium. A chromatographic method utilising a column of cellulose has also been described, which again, while being widely applicable and capable of giving accurate results, is time-consuming.[9] In an earlier paper[10] mention was made of the possibility of separating tantalum and niobium from each other and from titanium by partition chromatography on a strip of paper, with a mixture of ethyl methyl ketone and hydrofluoric acid as solvent. This observation has formed the basis of the work described in this report. A method has been designed for a chromatographic separation on a strip of paper that permits a single operator to carry out some 70 niobium determinations per day on a variety of materials.

Essentially, the method consists of spotting a fluoride solution of the sample on to a strip of filter-paper and then chromatographing with a solvent mixture of ethyl methyl ketone, hydrofluoric acid and water with upward diffusion of the solvent. After evaporation of the solvent the strip is made alkaline by exposing to ammonia vapour and sprayed with an aqueous solution of tannic acid. The niobium is located as an orange-yellow band near the solvent front. The quantity of niobium present is determined by comparison of the intensity and area of the band with that produced on standard strips prepared with known quantities of niobium. The breakdown of the sample is produced either by direct attack with hydrofluoric acid, or by fusion with potassium bisulphate followed by solution of the melt in hydrofluoric acid. The chromatographic separation is carried out on ten samples simultaneously. This is achieved by cutting slots from a cylinder of Whatman's No. 1 filter-paper so as to leave ten strips joined together at top and bottom. The cylinder is placed vertically in a polythene beaker containing about 20 ml of the ketone solvent and covered with a Petri dish. The solvent diffuses up the paper and in 20 minutes the separation is complete. The cylinder of paper is removed and, after exposure to ammonia vapour, is sprayed with a dilute solution of aqueous tannic acid. A photograph of the type of separation achieved is shown in Fig. 1. The separation of two samples is shown, together with a range of standards produced with known niobium solutions. Under the recommended conditions few metals move from the original sample spot and of these only tantalum moves as far up the strip as niobium. With all the solvent mixtures so far examined, tantalum was found to move in a narrow band in the solvent front. It gives, however, only a slight yellow colour with tannic acid and normally does not materially interfere with the niobium determination.

For samples in which tantalum is in sufficient excess to interfere, it is possible to modify the solvent so as to give a distinct separation of niobium and tantalum in which the tantalum is in the solvent front and niobium some way behind it.

The method has been applied to a number of pyrochlore-bearing soils, to various minerals containing ilmeno-rutile, to pyrochlore-bearing granites and to samples of steel, with satisfactory results in all cases. For samples containing more than 0·10 per cent. of niobium pentoxide the accuracy is ±10 per cent. For lower-grade samples the accuracy decreases, and a modified procedure, which will be described in a later paper, is recommended. The modified procedure was designed for geochemical prospecting samples and permits the determination of as little as 0·0004 per cent. of niobium pentoxide. For samples containing between 0·1 and 0·01 per cent. of niobium pentoxide the accuracy is ±20 per cent.

PREPARATION OF SAMPLE SOLUTION

The weight of sample taken for analysis depends on the niobium content, but should not exceed 1 g. The method used to get the sample into solution varies with the type of material being treated. For pyrochlore-bearing minerals, when it can be assumed that complete solution of the niobium is possible by treatment with hydrofluoric acid, 1 g or less of the finely ground sample is weighed into a small platinum dish, treated with about 5 ml of 40 per cent. w/v hydrofluoric acid, and the mixture is evaporated to dryness on a water-bath. More severe heating should be avoided as this leads to the formation of a hard cake that is difficult to crush. Where large numbers of samples are involved, the platinum dishes can be replaced by 10-ml polythene beakers. Suitable beakers are readily fashioned from a block of polythene by machine-turning. By means of a suitable rim support, beakers of this type can be immersed in a bath of boiling water without visible signs of distortion, but heat transfer is poor and the time necessary for evaporation to dryness is four to six times that taken with a platinum dish. Exactly 2 ml of dilute hydrofluoric acid solution (25 ml of 40 per cent. w/v hydrofluoric acid and 75 ml of water) are added to the dry residue. This may most readily be carried out with the aid of a calibrated polythene pipette fitted with a rubber bulb. The mixture is stirred with a polythene rod to crush the cake and then the dish is covered and left to stand for 30 minutes.

For samples in which the niobium mineral is more refractory, *e.g.*, in samples of ilmeno-rutile, a potassium bisulphate fusion procedure is used. One gram or less of the sample is weighed into a platinum dish and a few drops of concentrated sulphuric acid together with a quantity of potassium bisulphate equivalent to four times the sample weight are added. The mixture is fused and, after cooling, the melt is treated with 5 ml of 40 per cent. w/v hydrofluoric acid and evaporated to dryness. The residue is treated with exactly 2 ml of dilute hydrofluoric acid, as described for pyrochlore-bearing samples. It is found that with some samples the addition of 2 ml of dilute hydrofluoric acid results only in a thick paste from which little or no supernatant liquid separates. For these samples the volume of dilute hydrofluoric acid added is increased to 4 ml.

Samples of steel containing niobium present a special problem. When the steel is readily soluble in strong hydrofluoric acid, the sample can be treated by the procedure used for pyrochlore-bearing minerals. More usually it is found that quicker solution is attained by dissolving the steel in nitric acid containing hydrofluoric acid. As is explained later, this will result in the oxidation of any molybdenum present, which is undesirable. Then the nitrate solution is evaporated to dryness, treated with hydrofluoric acid and again evaporated to dryness. This removes most of the nitric acid, and the molybdenum is now reduced by addition of a little pure iron-wire and a further evaporation with hydrofluoric acid. The final residue is treated with 2 ml of dilute hydrofluoric acid as described already for other samples.

CHROMATOGRAPHIC SEPARATION

For the chromatographic separations, specially cut paper strips that permit the simultaneous running of ten samples are used. For the present work these were cut by hand from Whatman's No. 1 filter-paper sheet, but suitably prepared material is now available commercially. Large sheets of paper are cut into rectangles, $4\frac{1}{2}$ inches × 9 inches. Slots $3\frac{3}{4}$ inches long and $\frac{1}{10}$ inch wide are cut parallel to the short side leaving $\frac{3}{8}$ inch uncut at each end. The slots are cut at $\frac{3}{4}$ inch intervals to produce 11 strips $\frac{3}{4}$ inch wide and a strip at one end of the sheet a little less than $\frac{3}{4}$ inch wide. The choice of strip width may be varied

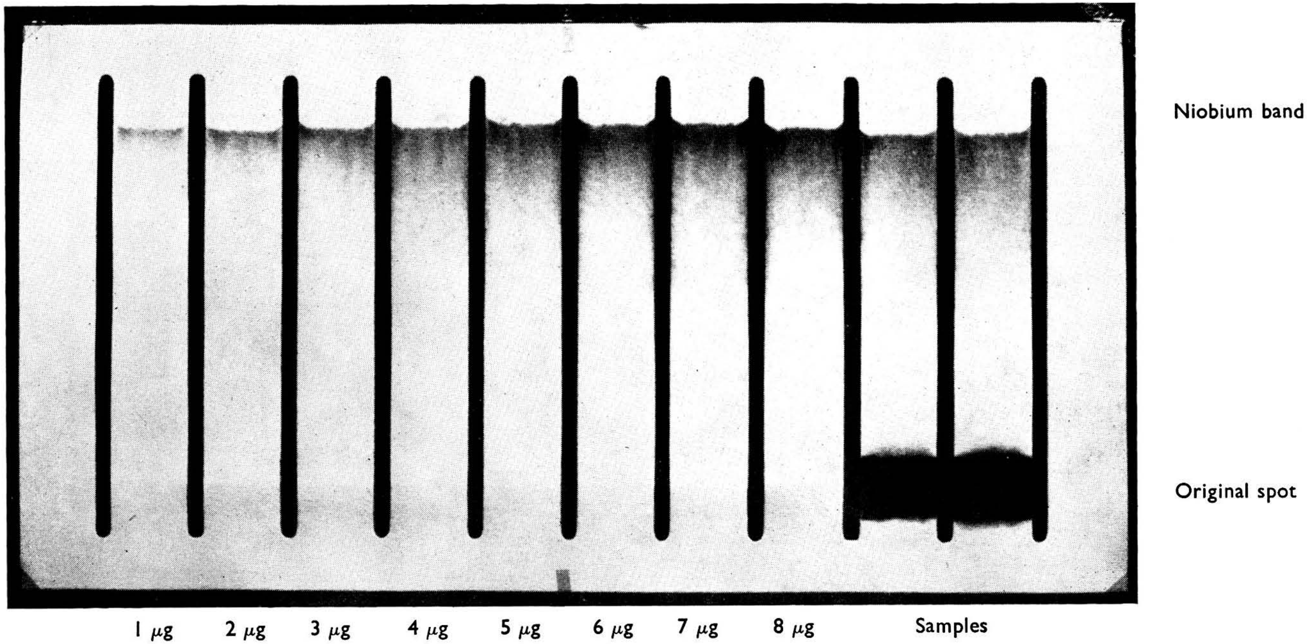

Fig. 1. The chromatographic separation of niobium

to suit the purpose of the operator, but all strips with the exception of the one at each end of the sheet must be identical in every respect. After standing for 30 minutes, the sample, prepared in 2 ml of diluted hydrofluoric acid as already described, will be covered by a layer of clear supernatant liquid. With the aid of a glass capillary pipette, 0·01 ml of this liquid is place near to one end of a strip. Suitable pipettes may be prepared by drawing out a piece of glass tubing to a capillary at one end and calibrating at 0·01 ml. The capillary bore should be such that the liquid will rise by capillarity to the 0·01-ml graduation on immersing the end in the sample solution. This type of pipette is easily produced and it can be used for some time before attack by hydrofluoric acid necessitates its being discarded. The sample solution is placed on the strip by drawing the pipette right across the strip so that the wet area forms a rectangular patch just at the bottom of the strip, but does not extend into the bottom portion of the paper that joins the strips. Ten sample solutions can be placed on one sheet of paper. The two end strips are not used.

The sample spots are allowed to dry. This can be carried out by leaving the sheet in the open for 1 hour, but more consistent results, particularly in atmospheres of high humidity, are attained by drying the strips in an atmosphere of controlled humidity. The strips may be dried by standing them inside a closed vessel over saturated potassium carbonate solution containing an excess of solid carbonate. This is easily arranged by placing a 100-ml beaker, containing the potassium carbonate slurry, inside a 600-ml beaker fitted with a cover. This maintains an atmosphere of 44 per cent. relative humidity at room temperature and will also tend to neutralise any hydrofluoric acid that evaporates from the paper. It has been found that both the water and hydrofluoric acid concentrations influence the nature of the niobium bands. The moisture content of the filter-paper depends upon the humidity of the surrounding atmosphere, so that by controlling the drying conditions both the water and acid in the original spot and the moisture content of the remainder of the strip are standardised.

After drying, the sheet is bent round to form a cylinder, with the two end strips overlapping and fastened at the top with a paper-clip. The cylinder is then stood, sample spots lowermost, in a 600-ml polythene beaker containing about 20 ml of organic solvent mixture. The beaker is covered with a 4½-inch diameter Petri dish. Care should be taken to see that the cylinder of paper stands free from contact with the sides of the beaker. The edges of the strips should not touch each other. A useful technique is to make a slight fold half-way along each strip so that the cylinder bulges slightly outwards under its own weight.

The organic solvent mixture consists of a mixture of ethyl methyl ketone with hydrofluoric acid and water. The ketone used should be both pure and dry. Commercial ethyl methyl ketone may be sufficiently purified for the purpose by heating under a reflux condenser 700 ml of the ketone with 100 ml of an aqueous solution of alkaline permanganate (2 g of potassium permanganate + 3 g of sodium bicarbonate per 100 ml of water). After heating for 3 hours the ketone is separated, dried with calcium chloride, then with caustic soda and finally redistilled. The pure ketone keeps well and one Winchester quart is sufficient for 6000 to 7000 determinations. The movement of niobium from the test spot is dependent on the concentration of hydrofluoric acid and water in the solvent. With high acid concentrations, the niobium is extracted in a very narrow band in the solvent front. Use is made of this in detecting trace amounts of niobium in soils by the modified procedure to which reference has already been made. As the quantity of niobium present increases, it becomes progressively more difficult to determine the niobium by visual comparison with a standard. For this reason, in the present work, a solvent has been chosen that extracts niobium in a band that trails back from the solvent front. The niobium is thus spread over a larger area and comparison becomes easier. A suitable solvent is ethyl methyl ketone containing 8 per cent. v/v of water and 4 per cent. v/v of 40 per cent. w/v hydrofluoric acid. This gives satisfactory standards over the range 0 to 20 μg of niobium pentoxide. If each standard differs from the next by 2 μg of niobium pentoxide, it is possible to match an unknown sample or place it between two standards, *i.e.*, to determine to within 1 μg of niobium pentoxide. This solvent is suitable for use over a temperature range of 20° to 25° C. For higher temperatures it is necessary to reduce the amount of hydrofluoric acid in the solvent to get comparable bands. The solvent may be made up in bulk and stored in a screw-cap polythene bottle. No signs of deterioration were observed on keeping the solvent for several days. The 20 ml of solvent placed in the beaker may be used for five or six sheets, *i.e.*, for 50 or 60 separations, and should then be replaced. A second solvent has been used when a greater accuracy has been required over the range 1 to 10 μg. With 1·5-cm wide strips instead of the ¾-inch wide type already described and a solvent consisting of ethyl methyl ketone + 5 per cent. v/v of 40 per cent. w/v hydrofluoric acid + 4 per cent. v/v of water it is possible to prepare a satisfactory range of standards in 1 μg steps from 1 to 10 μg. The separations shown in Fig. 1 were produced with this second set of conditions. This solvent is best used at 25° C. At 20° C the water content of the solvent must be increased to 5 per cent. v/v for comparable bands. These small variations in acid and water content of the solvent are made in order to ensure that the shape and area of the niobium bands are as reproducible as possible.

Detection of niobium and comparison of stains

After completion of the chromatographic separation, the niobium is detected as an orange - yellow colour by exposing the filter-paper sheet to ammonia vapour and spraying it with aqueous tannic acid. The sheet may be made alkaline conveniently by removing the paper cylinder from the beaker of solvent, allowing the solvent to evaporate and then standing the cylinder in a covered 600-ml beaker containing a small beaker of ammonium hydroxide, sp.gr. 0·880. After a few minutes the cylinder is taken out of the beaker, the paper-clip is removed and the sheet is sprayed, with the aid of an atomiser spray,[11] with a 2 per cent. w/v aqueous solution of tannic acid. If a compressed-air line is not available, an atomiser of the scent-spray type may be found suitable for distributing the aqueous tannic acid. If the spraying is carried out before the ammonium hydroxide treatment a dark uneven background is likely to be formed on the paper. After spraying, the strips are dried, preferably by warming under infra-red lamps. The niobium is found as an orange - yellow complex near the solvent front. The intensity of colour increases a little on standing overnight and then remains constant. Strips have been kept for several weeks without deterioration. If standard strips are prepared on the same day as the samples, comparison may be made immediately after drying. If the standards are prepared less frequently, comparison should be made after the strips have been left overnight.

Determination of the niobium is made by comparing the stain from a sample strip with those produced by a series of standards. Comparison is best made by viewing the strips by transmitted daylight. With strips 1·5 cm wide and a series of standards each differing from its neighbour by 1 μg over the range 1 to 10 μg a sample can be assayed to within 0·5 μg.

An attempt was made to measure the density and area of the niobium stains by physical means. A densitometer was constructed in which the light transmitted by a given area of the strip, which included the niobium stain, was measured with the aid of a photo-electric cell. With a blue filter having a transmission peak at about 450 mμ, the sensitivity was as desired, but with the present design of instrument results were somewhat more erratic than those from visual comparison. It is hoped that with suitable modification a precision at least equal to that attained by the eye will be achieved.

Preparation of standards

Standard solutions of niobium may be prepared in the following manner. A quantity of Specpure niobium pentoxide is heated in a crucible at 500° to 600° C for 30 minutes and then allowed to cool in a desiccator. Exactly 0·500 g of the ignited oxide is weighed into a platinum dish and warmed with a mixture of hydrofluoric and nitric acids until solution is complete. The solution is evaporated to dryness and then evaporated to dryness twice more with further hydrofluoric acid. The residue is dissolved in the minimum amount of warm hydrofluoric acid and then allowed to cool. The solution is diluted and transferred to a 100-ml calibrated flask. The solution is diluted to the mark with water and transferred to a polythene bottle as quickly as possible. This solution contains 50 μg of niobium pentoxide per 0·1 ml. The required range of standards is prepared from this stock solution by dilution with water. All the standard solutions are kept in screw-capped polythene bottles.

Method

Reagents—

Hydrofluoric acid, 40 per cent. w/v.

Hydrofluoric acid, diluted—Mix 1 volume of 40 per cent. w/v hydrofluoric acid with 3 volumes of water.

Potassium carbonate—A saturated solution containing an excess of the solid carbonate.
Ammonium hydroxide, sp.gr. 0·880.
Tannic acid—A 2 per cent. w/v solution in water.
Nitric acid, sp.gr. 1·42.
Iron wire.
Potassium bisulphate—Powdered solid.
Standard solutions of niobium—The standard solutions are in dilute hydrofluoric acid.
Filter-paper—Whatman's No. 1 paper.

PROCEDURE FOR PYROCHLORE-BEARING MATERIALS—

Weigh 1 g of a suitably ground sample into a 10-ml polythene or platinum beaker. The sample weight should not exceed 1 g and may be considerably less for higher-grade materials. Add 5 ml of concentrated hydrofluoric acid and evaporate the mixture to dryness on a water-bath. Add 2 ml of diluted hydrofluoric acid solution by means of a polythene pipette fitted with a rubber bulb. Stir with a polythene rod and leave for 30 minutes. Remove 0·01 ml of the supernatant liquid with a glass pipette and deliver it to one end of a Whatman's No. 1 filter-paper strip. Add a series of standard niobium solutions to similar paper strips. The volume of standard solution added to each strip must be the same as that used for the sample, namely, 0·01 ml. Allow the strips to dry for 1 hour over saturated potassium carbonate solution. Prepare the solvent by adding 4 ml of 40 per cent. w/v hydrofluoric acid and 8 ml of water to 88 ml of ethyl methyl ketone. Pour about 20 ml of the solvent into a 600-ml polythene beaker 30 minutes before the drying of the paper strips is complete. Cover the beaker with an inverted 4½-inch diameter Petri dish. Bend the sheet of strips to form a cylinder and clip it at the top with a paper-clip, then place it in the solvent beaker with the sample spots lowermost. Allow the solvent to diffuse upwards and remove the strips just before the solvent front passes round the upper end of the slots between the strips. Allow the solvent to evaporate. Expose the sheets to ammonia gas until alkaline and then spray them with 2 per cent. aqueous tannic acid. Spray both sides of the sheet evenly. Allow the strips to dry and compare the niobium bands due to the samples with those of the standards.

PROCEDURE FOR NIOBIUM STEELS—

Weigh 0·1 to 1 g of steel into a platinum dish. Add 5 ml of water, 5 ml of nitric acid, sp.gr. 1·42, and 2 ml of 40 per cent. w/v hydrofluoric acid, and evaporate the mixture to dryness on a water-bath. Repeat the evaporation with mixed acids, if the decomposition of the steel is not complete. Add 5 ml of 40 per cent. w/v hydrofluoric acid and evaporate to dryness. Add 0·3 g of pure iron wire and 5 ml of 40 per cent. w/v hydrofluoric acid, and again evaporate to dryness. Add 2 ml of diluted hydrofluoric acid. Stir the mixture and allow it to stand for half an hour. Carry out chromatography of the supernatant liquid as already described for pyrochlore-bearing minerals.

PROCEDURE FOR REFRACTORY MINERALS—

Weigh up to 1 g of sample into a small platinum crucible. Add four times the sample weight of potassium bisulphate. If the sample weight is less than 1 g, a greater excess of bisulphate can be used, but the weight of bisulphate must not exceed 4 g. Heat gently at first to avoid spitting and then to red heat. If the melt is not clear when the evolution of sulphur trioxide ceases, allow the melt to cool, add a few drops of concentrated sulphuric acid and repeat the fusion. Allow the melt to cool, add 5 ml of 40 per cent. w/v hydrofluoric acid and evaporate the mixture to dryness. Add 2 ml of diluted hydrofluoric acid to the residue. Stir the mixture and let it stand for half an hour. Carry out chromatography of the supernatant liquid as already described for pyrochlore-bearing minerals.

THE EFFECT OF OTHER ELEMENTS

The behaviour of a number of metals during the chromatographic procedure has been investigated. With the conditions recommended in the method, the following metals do not move from the test spot: Mn, Cu, Ag, Sn, Pb, Hg, Ce, Cr, Fe, W, Al, Ba, Sr, Ca, Mg, Ni, Th, U, Zn, Co and the rare earths.

The following metals move to a greater or lesser extent—

Titanium—Titanium has been present in nearly all the samples dealt with. After spraying the strip with tannic acid reagent, it appears as a bright orange band that is just moving from the test spot. The maximum movement of titanium was on a sample of ilmenorutile, where the leading edge of the titanium band was only 8 mm in front of the edge of the sample spot.

Zirconium—Zirconium behaves similarly to titanium and moves partially out of the test spot. It does not, however, give a colour with the tannic acid reagent and is not detected unless specially tested for.

Antimony—Antimony moves just clear of the test spot, R_F value = 0·2, but gives no colour with tannic acid.

Vanadium—The movement of vanadium is similar to that of antimony. It has an R_F value of 0·17 and is detected as a grey-black band on spraying with aqueous tannic acid.

Molybdenum—The behaviour of molybdenum varies according to its valency state. In its higher valency state it is detected on spraying with aqueous tannic acid as a brown stain that overlaps the yellow-orange band due to niobium. In its reduced state the movement of molybdenum is less, R_F value = 0·35, and it forms a band well separated from and behind that due to niobium. During the examination of molybdenum-bearing steels it was found necessary to take precautions to prevent interference by molybdenum in the niobium determination. If the steel sample was dissolved in hydrofluoric acid, the molybdenum was reduced and did not move sufficiently far to interfere with the detection of niobium. When nitric acid was used to assist in the solution of the steel, however, it was found necessary to evaporate the solution to dryness, to re-evaporate with hydrofluoric acid to remove nitric acid and then, after the addition of a little pure iron wire or filings to the residue, to repeat the evaporation with hydrofluoric acid.

Tantalum—This is the only significant cation that has been found to move along the strip with a rate comparable with that of niobium. With all the solvent mixtures used, tantalum moved in the solvent front. If present in sufficiently large amounts it is detected as a thin pale yellow line at the limit of solvent movement. The colour formed by tantalum with aqueous tannic acid is too faint for it to have any serious effect on the niobium separation. By variation in the acid and water content of the solvent it is possible to separate niobium and tantalum. The tantalum travels in the solvent front separated from niobium, which has an intermediate position between the original spot and the tantalum band. A further paper will deal with the separation and determination of tantalum by a paper-strip method.

Anions—The chromatographic separation is unaffected by reasonable amounts of a number of anions. The Sukulu-soil samples contain a large proportion of phosphate, which does not impede the extraction of niobium. Sulphate may be present in very large quantities as is so when a fusion with bisulphate has been used to break the sample down. In the same manner nitric acid can be used in the breakdown step without harmful effects. Chloride should not be present as it promotes the movement of iron but, even in the presence of a large amount of chloride, the iron does not move in the solvent front.

APPLICATION TO PYROCHLORE-BEARING MATERIALS

The method has been applied to a number of samples in which the niobium was present as pyrochlore. It has been assumed that, with these samples, solution of the niobium is complete on treatment of the sample with hydrofluoric acid. Results on soils of this type from the Sukulu area of Africa are shown in Table I. Solution of the samples in hydrofluoric acid was carried out on two separate portions of each soil. On the first solution two and on the second solution three chromatographic separations were carried out. Each strip was compared with standards by two operators as indicated in the table. The mean result in each case compares favourably with results determined by a cellulose-column method.[12] Samples C, D and E have been examined in a number of laboratories by a variety of methods, including gravimetric, spectrographic and colorimetric procedures. The mean results have been included in the table as standard figures. The sample solution for samples A, C and D consisted of 2 ml of diluted hydrofluoric acid. For sample B this was increased to 4 ml and for sample E to 6 ml of the diluted hydrofluoric acid, in order to bring the sample within the standard range.

TABLE I

NIOBIUM PENTOXIDE IN SUKULU SOILS BY THE PAPER-STRIP METHOD

Determination	Operator	Niobium pentoxide found in Sample A, %	Sample B, %	Sample C, %	Sample D, %	Sample E, %
1. Strip 1	X	0·22	0·56	0·18	0·20	0·68
	Y	0·24	0·44	0·14	0·18	0·50
Strip 2	X	0·20	0·44	0·16	0·18	0·56
	Y	0·24	0·52	0·16	0·18	0·62
2. Strip 1	X	0·20	0·48	0·16	0·18	0·60
	Y	0·24	0·48	0·14	0·16	0·48
Strip 2	X	0·20	0·48	0·16	0·18	0·54
	Y	0·26	0·48	0·18	0·22	0·72
Strip 3	X	0·22	0·48	0·14	0·18	0·60
Mean	. .	0·22	0·48	0·16	0·18	0·59
By chromatographic column	. .	0·25	0·45	0·19	0·19	0·60
Standard	. .	—	—	0·16	0·21	0·60

Two samples of Nigerian granite containing pyrochlore were also examined, the sample being dissolved in hydrofluoric acid with satisfactory results, as shown in Table II.

TABLE II

THE DETERMINATION OF NIOBIUM PENTOXIDE IN NIGERIAN GRANITE

Sample	Niobium pentoxide found by comparison of same strip by different operators A, %	B, %	C, %	D, %	Mean Nb_2O_5 found, %	Nb_2O_5 found by column method,[12] %
Granite 1	0·24	0·22	0·26	0·26	0·24	0·22
2	0·26	0·26	0·28	0·28	0·27	0·25

APPLICATION TO NIOBIUM STEELS

The method has also been applied to a limited number of niobium-bearing steels. For this type of sample the method of solution was changed. Hydrofluoric acid attacked the steel somewhat slowly and on evaporation of the solution there was a strong tendency to form a hard cake, which broke up with difficulty on addition of further hydrofluoric acid. The samples dissolved readily in a mixture of 10 ml of 50 per cent. v/v nitric acid and 2 ml of 40 per cent. w/v hydrofluoric acid, and this method of solution was preferred. The solution of the sample was evaporated to dryness on a water-bath and then re-evaporated to dryness with 5 ml of 40 per cent. w/v hydrofluoric acid. In the absence of molybdenum, 2 ml of diluted hydrofluoric acid were added to the residue and, after stirring and standing, an aliquot of the supernatant liquid was used for chromatography in the normal manner. When present, molybdenum was in its oxidised form after the second evaporation and interfered with the niobium determination. To suppress the interference due to molybdenum, 0·3 g of pure iron wire was added to the residue from the evaporation with hydrofluoric acid and the mixture was again evaporated to dryness with 5 ml of 40 per cent. w/v hydrofluoric acid. The residue was dissolved in 2 ml of diluted hydrofluoric acid and the solution was used for chromatography as before. Results on two steels, one with and one without molybdenum,

TABLE III

THE DETERMINATION OF NIOBIUM IN STEEL

	Given composition Cr, %	Ni, %	Mo, %	Ta + Nb, %	Weight of sample, g	Volume of sample solution, ml	Nb found, %
Steel A	18	8	nil	0·94	0·3	2	0·91
Steel B	18	8	3	0·99	0·3	4	1·03

are shown in Table III. Although the number of steels examined is small, there appears to be no reason why the method should not be generally applicable to such samples.

APPLICATION TO REFRACTORY MINERALS

When dealing with refractory materials, direct treatment with hydrofluoric acid will not result in complete solution of the niobium. For these materials fusion with potassium bisulphate has been used to effect an initial breakdown. Up to 1 g of sample was fused with about four times its weight of potassium bisulphate. About 5 ml of 40 per cent. w/v hydrofluoric acid were added to the melt and the solution was evaporated to dryness. A known volume of diluted hydrofluoric acid was added to the residue and, after stirring to break up the cake and standing, an aliquot of the supernatant liquid was taken for chromatography. The method was first tried on a Sukulu soil of known niobium content with satisfactory results (see Table IV). Samples 2 and 3 were very refractory samples, while the soil sample 4 contained niobium both as pyrochlore and ilmeno-rutile. It is not suggested that the method could be used for the accurate determination of niobium in high-grade samples of tantalite - columbite, such as sample 5, but it does enable the order of the niobium content to be found quickly.

TABLE IV

THE DETERMINATION OF NIOBIUM PENTOXIDE IN REFRACTORY MINERALS

Sample	Weight of sample, g	Volume of sample solution, ml	Nb_2O_5 found, %	Known Nb_2O_5 content, %
1. Sukulu soil	0·5	4	0·56	0·60
2. Ilmeno-rutile	0·1	2	2·6	2·58
3. Ilmeno-rutile	0·1	4	2·4	2·55
4. Felspathic ferruginous soil . .	0·4	2	0·25	0·22
5. Tantalite - columbite	0·01	2	15·0	14·5 (approx.)

COMPARISON WITH COLORIMETRIC METHOD

A number of samples, supplied through the kindness of Mr. W. H. Bennett of the Colonial Geological Surveys, was examined for niobium. The results for the series of samples are compared in Table V with results, quoted with the permission of and obtained by the Colonial Geological Survey Laboratory, who used a colorimetric method developed at that laboratory.

TABLE V

COMPARISON OF THE CHROMATOGRAPHIC AND COLORIMETRIC METHODS

Sample	Niobium pentoxide found by paper-strip method, %	Niobium pentoxide found colorimetrically, %
1. Felspathic ferruginous soil	0·04	0·04
2. Ferruginous phosphatic soil	0·67	0·66
3. "	0·77	0·88
4. "	0·09	0·12
5. Ferruginous soil with Mn, Ba and rare earths	1·4	1·45
6.	0·24	0·29
7.	0·72	0·72
8. Subsoil with $BaSO_4$ and rare earths . .	1·5	1·58
9. Felspathic ferruginous soil	0·25	0·22 (Total)
"	0·15	0·18 (HF soluble)
10. Ferruginous silica rock	0·15	0·14

The samples are representative of residual and detrital soils and subsoils associated with African carbonatite deposits and include one rock sample (10) that is a ferruginous silica rock (silicified carbonatite). Pyrochlore is the principal niobium mineral present, but sample 9 does, in addition to pyrochlore, contain a more refractory niobium-bearing mineral, probably ilmeno-rutile. The agreement between the methods is excellent, particularly when it is realised that all the results shown are single determinations.

CONCLUSION

The method provides a simple and speedy procedure for the determination of niobium in a wide variety of materials with sufficient accuracy for many purposes. The consumption of chemicals is extremely small, one Winchester quart of solvent being sufficient for about 7000 determinations. Titanium, molybdenum and vanadium will be detected during the determination, if present in the sample. If it is shown that the molybdenum and vanadium present in the material are completely soluble in the hydrofluoric acid extract, it would probably be possible to determine both elements simultaneously with the niobium.

The authors wish to express their thanks to Mr. W. H. Bennett of the Colonial Geological Surveys for his co-operation and for permission to quote results supplied by him.

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RADIOCHEMICAL GROUP
CHEMICAL RESEARCH LABORATORY
TEDDINGTON, MIDDLESEX

January 29th, 1954

DISCUSSION ON THE FOREGOING FIVE PAPERS

MR. E. A. HONTOIR (Chief Chemist, Rio Tinto Co. Ltd., Port Talbot) said that it was just twelve months since he was confronted with the problem of analysing about 1500 Sukulu-soil samples within a period of about five months, and as results would be required in duplicate, approximately 3000 separate determinations would have to be made.

At that time the gravimetric methods were regarded as being somewhat long-winded and tedious. The preprint of the paper by Dr. F. H. Burstall and Mr. A. F. Williams on the application of chromatography to the determination of niobium in complex ores, later published in *Analyst*, 1952, **77**, 983, had been issued. Mr. Chirnside and his assistants had worked with this method and had kindly introduced him to the procedure they had evolved from it. He and his colleagues set about the problem of adapting this procedure to their needs. At first they could not make the method work, *i.e.*, to give concordant duplicates, but even when they did, it became apparent that a large team of analysts would be needed to do the required number of analyses.

They sought further assistance and advice, and as a result research was started to produce a spectrographic technique that would be likely to solve the problem. The paper produced by Messrs. Campbell and Nicholas was one result, but it naturally took time and a good deal of work to complete. In the meantime, Mr. A. R. Powell and his colleagues produced a gravimetric technique based on the original work done by them in collaboration with the late Dr. Schoeller, *i.e.*, the separation as a tannic acid complex, which produced a mixed oxide residue that contained Nb_2O_5, Ta_2O_5 and TiO_2. The TiO_2 was determined colorimetrically and the result was corrected accordingly.

They tried out this procedure and were able, after one or two modifications, to streamline the procedure, and they eventually found that they were able to work in batches of 36 separate determinations per chemist, each batch taking three days to complete, *i.e.*, the time per determination was approximately half an hour. They had used this method throughout and had completed the 3000 determinations. Although most of the samples were of Sukulu soil, they had done some work on mineral-dressing products.

When they had concentrates containing from 15 per cent. of $(Nb,Ta)_2O_5$ upwards, they checked the results by the chromatographic procedure, which had now been shortened by Messrs. Mercer and Wells, and had been described earlier that evening. By and large the results had agreed well, although they had not used a colorimetric finish, but had purified the niobium residue by one pyrosulphate - tannic acid separation.

They had found that, when making so many determinations at what he thought was a good rate, it had been necessary to make checks from time to time; generally speaking, they believed that results had been satisfactory.

They had tried the absorptiometric method, but their first results were not encouraging and they found themselves prevented from doing further work on it by lack of time. It was their intention to proceed further by using it in conjuction with the first stages of their gravimetric method.

The spectrographic methods were rapid and undoubtedly were most important. He did not know whether anyone had had experience of the fluorescent X-ray spectrographic technique that was, he believed, being used in the United States.

Referring again to the chromatographic methods, he said there was no doubt that the rapid method that had been evolved by Messrs. Hunt and Wells should be of the greatest use to geochemists working on the spot.

He would like, in conclusion, to congratulate the Society on the undoubted success of the evening and the authors of the papers for the excellent work that had been done. On behalf of the Rio Tinto Company he thanked all those who had co-operated in the work for the assistance that had been given.

MR. L. E. GARDNER (Chief Chemist, Edgar Allen & Co. Ltd., representing B.I.S.R.A.) said that it was a very great pleasure to come down from Sheffield to listen to these six papers on such an interesting subject. When he said "from Sheffield" it was obvious that he was mainly interested in the possible application of these methods to the determination of niobium and tantalum in steel. The class of steel to which niobium was usually added was the stainless materials, such as the 18 per cent. chromium - 12 per cent. nickel steels, but the determination might be complicated by the presence of tungsten and titanium. Niobium was also added to the permanent-magnet materials, which contained alloying amounts of cobalt, nickel, copper, aluminium and occasionally titanium. The methods used were usually based on the paper by Bagshawe and Elwell presented before this Society some years ago. The ferro-alloys had also to be examined, and with them they became more interested in the separation of niobium and tantalum, where the latter was usually present in amounts up to 10 per cent. of the niobium content. On one occasion they had had to deal with an alloy containing approximately 20 per cent. each of niobium, tantalum and titanium on which they had obtained reasonable results by the Schoeller and Powell procedures, but the chromatographic procedure of Williams had proved readily applicable to this class of material and gave very satisfactory results.

There were one or two queries he wished to put to the speakers. Mr. Milner had mentioned a recovery of niobium of 70 to 80 per cent., which did not influence his work as he used radiometric correction with niobium-95 tracer. He asked whether Mr. Milner thought, if they applied the principle of his method to steels, that they could improve on this recovery, as additions of tracers would be detrimental, particularly if they were not consistent. In the second paper by Mr. Marzys, he was not certain whether tungsten and titanium were major interfering elements or whether their interference could be overcome.

The spectrographic procedures of Mr. Campbell were very interesting, and obviously could give very rapid and accurate results; but he wished to know if the author had information as to the possibility of tungsten interference on the niobium line he used, and similarly whether titanium interfered on the tantalum line. He would have thought the niobium line at 3195 A would have been more useful.

The 3-inch column introduced by Mr. Wells to speed up the chromatographic procedure was a big step forward, but he asked if it was still necessary to carry out the lengthy treatment of ethyl methyl ketone before the procedure was carried out, as this was a rather tedious, time-consuming business. There is also the question of tungsten, and he asked Mr. Wells if the tungsten figures he had quoted were quantitative or if they just showed that some of the tungsten had been carried through the column. The application of paper-strip chromatography was apparently extremely sensitive, and he wondered if Mr. Wells thought it could be applied successfully to a series of steels containing 15 to 20 elements in residual amounts of the order of 0·0 to 0·10 per cent., which they had recently made for a special purpose. The determination of niobium and tantalum in these amounts presented quite a problem by normal methods.

Finally, he wished to thank the speakers for these very well presented papers and for giving them some new lines of attack to think about.

MR. W. RAMSDEN (British Non-Ferrous Metals Research Association) said that the spectrographic solution method developed at the British Non-Ferrous Metals Research Association for the determination of niobium and tantalum in Sukulu-type soils was similar to that described by Mr. Campbell, the porous cup electrode technique, originally described by C. Feldman (*Anal. Chem.*, 1949, **21**, 1041) being used. Acknowledgments were due to Mr. Campbell for advice given during the development of the method on the use of molybdenum as an internal standard and on the choice of line pairs.

The method of chemical extraction differed in some respects from that described by Mr. Campbell and was as follows. After boiling 5 g of the sample with 60 ml of concentrated hydrochloric acid and 0·5 g of potassium chlorate for 10 minutes, followed by further boiling with 40 ml of concentrated hydrochloric acid for 5 minutes, the mixture was diluted with water, and then it was boiled with saturated sulphur dioxide solution. More sulphur dioxide solution was added and the precipitate was filtered off and washed with hot water.

The residue was then ignited in a platinum dish and taken up in a mixture of 25 ml of hydrofluoric acid and 10 ml of concentrated sulphuric acid. The mixture was evaporated to fuming, cooled, and tipped into 50 ml of water, 7 ml of 100-volume hydrogen peroxide were added and the solution was filtered into a 100-ml calibrated flask. Then followed the addition of the molybdenum internal standard solution—0·02 g of molybdenum in 10 ml of concentrated sulphuric acid.

The solutions were clear and orange in colour, the main metallic constituents being titanium, niobium, aluminium and zirconium, with traces of iron, silicon, tantalum and molybdenum. Spectrographic examination of the rejected filtrates and residues from the solution revealed no trace of niobium or tantalum.

In the spectrographic technique the B.N.F.M.R.A. General Purpose Source Unit was used for excitation and the lines Nb 2698·8 A, Nb 2665·2 A, Ta 2400·6 A and Mo 2688·0 A were measured, there being no interference from titanium at these wavelengths.

At niobium contents of 0·1 per cent., the coefficient of variation of the niobium determination (for the mean of triplicate spectra) was 2 per cent. of the content and 10 per cent. of the content for tantalum at 0·03 per cent. The limit of detection for both niobium and tantalum was 0·01 per cent.

For one sample the preparation of the solution occupied 2 hours and the spectrographic determination 1 hour, but the additional time taken for further samples treated simultaneously would be small.

The spectrographic technique was well adapted to the determination of higher proportions of niobium in the soil, and could probably be used for concentrates and materials such as ferro-niobium, with appropriate modification of the chemical separation.

MR. A. H. BOWES (Murex Ltd., Rainham, Essex) asked Mr. Milner if he had any doubts as to the stability of the thiocyanate colour, whether the colour tended to fade fairly rapidly and whether it was necessary to measure the optical density immediately after the colour was developed.

MR. T. BURCHELL (Murex Ltd., Rainham, Essex) joined in expressing appreciation of the series of papers, which he felt sure would help not only in mineral analysis proper, but with the metallurgical products whose analysis was such a prime necessity to smelters like themselves. It was their function to smelt the concentrates resulting from the work of the miners and economic geologists, and produce metallic niobium in suitable form for the various metal industries, whether ferrous or non-ferrous. These products of high niobium content themselves presented quite a different analytical problem from that confronting the steelmaker with a fractional percentage in his steel, or on the other hand the mineral development team in the field, with their equally fractional niobium content. There were, however, other metallurgical control problems involving just such proportions, whether in slags or in intermediate products, in the solution of which the corresponding methods from the papers presented might well be very helpful.

They themselves were using the tannic acid method, assisted by more recent spectrographic procedures, and it seemed a proper occasion to acknowledge in the present company, including as it did Mr. A. R. Powell, the great value of the long series of investigations that Mr. Powell had made with Dr. Schoeller, and published over a period of years in *The Analyst.* This had indeed been the only light in many years of work with niobium, when most published methods were useless, and they were glad to say it was still their standard.

He would like to ask the authors of the present papers whether titanium was not in fact a more dangerous element, in interfering with niobium determination, than tungsten. Little had been said about titanium, but they had found it by far the most frequent cause of inaccuracy. It was possible that mineral surveys carried out before the past year or two ought strictly to be re-investigated, because of the serious possibility of analytical error in evaluating niobium contents of, say, 0·2 per cent. in millions of tons of rock, or alluvials, and the economic factors at the present time. It was very doubtful if anything sufficiently accurate on a wide basis of sampling had really been possible before the present methods were available.

MR. A. R. POWELL thanked earlier speakers for the tributes they had paid to the pioneer work of the late Dr. Schoeller and himself in the application of tannic acid to the separation and determination of niobium and tantalum. They had always found that the two most difficult elements to separate from the earth acids were tungsten and titanium. He (the speaker) believed that no better method of separating tungsten than that involving fusion with alkali carbonate and precipitation of the earth acids with sodium chloride or magnesia mixture had yet been described. The pyrosulphate - tannic acid method for separating titanium from the earth acids certainly had its disadvantages; precipitation of niobium was slow, setting aside overnight being essential for complete precipitation, and the niobium needed at least two precipitations if much titanium was present. Work in his laboratory had confirmed that the chromatographic method making use of 15 per cent. of hydrofluoric acid in ethyl methyl ketone efficiently eliminated all the titanium in one operation, but the tungsten distributed itself between the column and the eluate. For this reason he preferred to obtain a titanium - niobium - tantalum oxide mixture (contaminated with tungsten) by precipitation of the mixed oxides with tannic acid from a neutral oxalate solution, then to remove the tungsten (and phosphate, if present) as described above, and finally to dissolve the mixed oxides in hydrofluoric acid and to eliminate the titanium on the column.

The great disadvantage of the chromatographic method was the time consumed in eliminating the ketone and excess of hydrofluoric acid; he had found that this could be considerably speeded by pouring the eluate into about one-quarter its volume of water containing an excess of boric acid and the tannic acid necessary to precipitate the earth acids; the ketone could then be rapidly evaporated in glass vessels and the earth-acid precipitation completed by neutralisation with ammonium hydroxide. The tannic acid precipitate filtered readily under suction and, if washed with half-saturated ammonium chloride solution, the earth-acid oxide obtained on ignition was free from impurity.

Simple precipitation of the earth acids by ammonium hydroxide from a fluoride solution invariably yielded a product contaminated with fluoride that could be completely removed only by fuming with sulphuric acid; precipitation with tannic acid gave a product free from fluorine. Cupferron could be used to precipitate the earth acids, but it was not selective, the solution had to be kept cool and the precipitate had to be ignited very slowly; the tannic acid precipitation could be made selective and was always done in hot solutions, and the precipitate was readily separated and gave no trouble on ignition. For these reasons he considered that the best way to determine the earth acids in steels was to obtain a nearly neutral sulphate solution and precipitate the earth acids and titania with tannic acid directly; although the oxides obtained were impure, they could readily be freed from tungsten by fusion with potassium carbonate, and the earth acids recovered from this treatment could be separated directly by chromatography.

The colorimetric method with pyrogallol appeared to be a useful, accurate and rapid method for determining small quantities of the earth acids and seemed to have several advantages over the thiocyanate method, especially as fewer elements interfered. In some preliminary tests he had made with this method he had obtained very satisfactory results in determining the earth acids in Sukulu soils. He felt, however, that for ores with a high content of earth acids, *e.g.*, tantalite and columbite, the chromatographic method was more accurate. Undoubtedly Mr. Wells and his collaborators were to be congratulated on making such outstanding advances in the analysis of this very difficult group of elements.

MR. W. H. BENNETT said that, during the last two years, the Mineral Resources Division of the Colonial Geological Surveys had been called on to determine niobium in a large number of samples of soils of the Sukulu type and related materials. At first a gravimetric method was used to estimate total earth acids. This involved a preliminary leach in diluted hydrochloric acid (1 + 1), followed by a modified pyrosulphate - tannic acid procedure, but although results were satisfactory, a more rapid method was required.

For various reasons they did not favour the thiocyanate method, but decided to investigate the hydrogen peroxide method for niobium. Mr. R. Pickup improved the sensitivity and selectivity of the procedures described in the literature by developing the colour in 80 per cent. sulphuric and 20 per cent. phosphoric acids, and described the method, which has now given satisfactory results with a large number of samples, in *Colonial Geology and Mineral Resources*, 1952, **4**, 358.

There was still much work to be done on separations involving the earth acids and related elements, and the procedures that had been described during the evening should assist in checking the older methods and in investigating new ones.

The meeting had been most successful. An encouraging feature was the large number of visitors present, including geologists, who depended so largely on the co-operation of chemists in mineral investigation work.

He would like to ask Mr. Wells if he had obtained a figure for the ratio of niobium to tantalum in Sukulu soils in the course of the investigation of his colorimetric method.

MR. B. BAGSHAWE asked for Mr. Milner's opinion on the potentialities of the thiocyanate reaction as a basis for the determination of niobium in steel.

At first sight it would seem that its application to steel analysis might be simpler than its application to low-grade African minerals. The niobium content range was broadly of the same order, *i.e.*, 0·2 to 3 per cent., but solution of the steel sample and preliminary isolation of the niobium and development of suitable conditions for the colour reaction appeared to present fewer problems. For example, by taking advantage of the high sensitivity of the thiocyanate reaction, it should be possible to operate on 10-mg aliquots from separations based on an initial 0·2 or 0·5 g of steel. By comparison, the existing methods, based on conventional chemical separation procedures, whilst satisfactory, were tedious, cumbersome and somewhat involved, and moreover must be operated on large sample weights (5 to 10 g) to give the required accuracy.

He had in mind that a simple separation on a 50-mg steel sample could probably be made by means of cupferron. This would give a quantitative yield of niobium (and tantalum); titanium, if present, would also be precipitated, together with some iron, and possibly also some tungsten and molybdenum, if these elements were present. According to Freund and Levitt there was no interference from titanium or tungsten when the weight ratio of WO_3 or TiO_2 to Nb_2O_5 was as much as 1 to 1. This would rarely arise with steels, as, with one or two special exceptions, niobium steels contained only incidental amounts of titanium or tungsten. Further, it might be possible to prevent tungsten interference by forming a complex with fluoride before precipitation with cupferron.

MR. MILNER, in reply to Mr. Gardner and Mr. Bagshawe, agreed that the procedure described by Mr. Smales and himself for niobium in low-grade African minerals might be modified to simplify the difficult problem of determining this element in steels. They had made some experiments on this problem, and the results would be published in a separate paper. It had to be stressed, however, that this type of procedure did not give the tantalum content of a steel, whereas the gravimetric procedure in use in this country gave the combined niobium and tantalum content.

In reply to Mr. Bowes, he said that the optical density of the thiocyanate colour for a solution containing 40 μg of niobium had remained reasonably constant over a period of about 20 minutes.

MR. WELLS, in reply, said that it was necessary to use pure ethyl methyl ketone for the chromatographic separation. Commercial ethyl methyl ketone required a treatment with alkaline permanganate followed by drying and redistillation. It was the practice at the Chemical Research Laboratory to treat the solvent in bulk and to store it until it was required. The purified solvent was stable over long periods.

In the column procedure, the figures quoted for tungsten were quantitative estimations of the amount of tungsten extracted with the tantalum and niobium. The total tungsten present was not by any means completely extracted.

The chromatographic-strip method should be applicable to steels containing 0·0 to 0·10 per cent. of niobium. The procedure described in the paper that had been presented would give results for amounts of niobium down to 0·02 per cent. A modified procedure, which they hoped to publish later, would permit as little as 0·0004 per cent. of niobium to be determined. This further publication would also contain details for the determination of small amounts of tantalum.

No trouble was experienced with titanium in the chromatographic method. By the paper-strip technique, separation of niobium and tantalum from both titanium and tungsten was readily achieved. By the column procedure, separation of niobium and tantalum from titanium was attained provided the test solution contained an excess of ammonium fluoride; separation from tungsten was only partial, as a trace of this element was extracted with the niobium and tantalum.

MR. MERCER said that they had not directly determined the ratio of niobium to tantalum in Sukulu-soil samples, but in concentrates produced by physical methods from such soils the ratio was about 12 to 1.

MR. MARZYS, in a written reply to Mr. Gardner's query, referred to Table I of his paper, which showed that the effect of tungsten was serious; but tungsten was rarely or never found in appreciable amounts in Sukulu-type soils, and he had only found it in Nigerian granite. A modification of the procedure to correct for the presence of tungsten was described in the paper (p. 337).

Titanium was, of course, a constant companion of niobium and tantalum in all their minerals, and the thiocyanate method had been chosen principally because it was the only method in which the titanium interference was small, as could be seen from Table I. This point had been stressed in the introduction to the paper, where it was mentioned that in all other colorimetric methods the effect of titanium exceeded that of niobium; this precluded their use for low-grade ores where titanium was usually more abundant than niobium. Sometimes the titanium could be suppressed by drastic means, for instance by using a concentrated sulphuric acid medium in the peroxide method, but that method was many times less sensitive than the thiocyanate procedure. The small interfering effect of titanium had been obviated by the use of a correction, described in the procedure, which could be dispensed with in routine work except when excessively large amounts of titanium were present (see p. 335).

The Volumetric Determination of Aluminium in Non-ferrous Alloys

BY G. W. C. MILNER AND J. L. WOODHEAD

The determination of aluminium can readily be accomplished by a volumetric procedure involving the addition of an excess of a standard ethylenediaminetetra-acetic acid solution to the aluminium solution followed by titrating the reagent unused in the formation of the aluminium - ethylenediaminetetra-acetic acid complex. A standard iron solution is used for this titration and salicyclic acid is a suitable indicator for showing the titration end-point. With this procedure it is possible to determine up to 60 mg of aluminium with an accuracy of better than ±1 per cent. This titration has proved advantageous in the rapid analysis of various non-ferrous materials including copper, zinc and magnesium-base alloys after the preliminary separation of the aluminium as its insoluble benzoate.

THE only widely used volumetric method for the determination of aluminium in non-ferrous materials involves the precipitation of the aluminium with 8-hydroxyquinoline followed by a bromate titration to determine the 8-hydroxyquinoline content of the precipitate. Milner and Townend[1] used this technique for the determination of aluminium in copper-base alloys after the initial separation of the aluminium, as its insoluble benzoate, from the other alloy constituents. More recently a British Ceramic Research Association Committee[2] recommended procedures for the determination of aluminium oxide in refractory materials by the precipitation of the aluminium with 8-hydroxyquinoline followed by bromate titration.

In the routine determination of aluminium in non-ferrous materials, however, an appreciable saving in time would result if the aluminium could be titrated directly instead of by way of its 8-hydroxyquinoline derivative.

Schwarzenbach's basic data on the complexes formed by ethylenediaminetetra-acetic acid with aluminium, copper, cadmium, zinc, nickel and lead were used by Přibil *et al*[3] in developing volumetric methods for the determination of these elements. The technique consisted in buffering the solution of the element with ammonium acetate in the pH range 5 to 6, adding an excess of a standard EDTA solution, followed by the potentiometric titration of the excess of EDTA not required for complex formation with a standard ferric chloride solution. Under these conditions it proved possible to determine the above individual elements in the presence of moderate concentrations of calcium, strontium and barium. Flaschka[4] also has developed volumetric methods for some of the above elements.

Although the EDTA titration is not specific for aluminium, it should be of value in non-ferrous analysis in which it is possible to separate aluminium from many other elements by precipitating it as benzoate. As ferrous salts do not form an insoluble benzoate, interference by iron with the EDTA determination of aluminium can be avoided by conducting the benzoate precipitation in the presence of thioglycollic acid[5] to keep iron in the reduced state. Other elements known to produce precipitates under these conditions are titanium, zirconium, hafnium, thorium and beryllium.[6] Fortunately none of these elements is normally present in non-ferrous alloys, such as copper, zinc and certain types of magnesium-base alloys, and no difficulties should arise in the analysis of these materials. Moreover, for the application of a volumetric method of this kind to routine analysis, a visual method of detecting the end-point of the titration would be preferable to the potentiometric technique. Details of suitable procedures for the rapid determination of the aluminium contents of non-ferrous alloys are given in the experimental section.

EXPERIMENTAL

Preliminary experiments were directed to the replacement of the potentiometric end-point by a visual indicator method for the titration of the excess of EDTA with standard ferric chloride solution. As both salicylic acid and pyrocatechol produce coloured complexes with free ferric ions in solutions of about pH 6, either of these reagents could be used as an indicator. As salicylic acid gave the stronger colour, it was used in this investigation. The suitability of salicylic acid as a visual indicator was confirmed by taking a known amount of a 0·1 *M* ferric chloride solution and adding an excess of a 0·1 *M* EDTA solution. After addition of 3 g of ammonium acetate, the pH value was adjusted to 6 with dilute ammonium hydroxide and the excess of EDTA was titrated with the 0·1 *M* ferric chloride solution in the presence of about 0·20 g of salicylic acid. At the titration end-point the colour of the solution changed from yellow to brown and the indication was that the reaction proceeded in accordance with the expression—

$$\text{Fe}^{\cdots} + \text{H}_2Y'' \rightarrow \text{Fe}Y' + 2\text{H}^{\cdot} \qquad \text{.. .. ..} \qquad (1)$$

$$\text{where } Y'' = \begin{array}{l} \text{CH}_2\text{N(CH}_2\text{COOH)(CH}_2\text{COO}') \\ | \\ \text{CH}_2\text{N(CH}_2\text{COOH)(CH}_2\text{COO}') \end{array}$$

On extending this technique to standard aluminium solutions by adding an excess of EDTA to form a complex with the aluminium and then titrating the excess of EDTA with the standard ferric chloride solution, the results were low for aluminium and the titration did not comply with the reaction—

$$\text{Al}^{\cdots} + \text{H}_2Y'' \rightarrow \text{Al}Y' + 2\text{H}^{\cdot} \qquad \text{.. .. ..} \qquad (2)$$

The results indicated that the aluminium was not reacting completely with the EDTA. Titrations were carried out at pH 5 to find out if the reaction became more quantitative at lower pH values. In these circumstances the ferric ions used in the titration were found to displace the EDTA from the aluminium complex in addition to combining with free EDTA in solution, indicating a reaction of the type—

$$\text{Fe}^{\cdots} + \text{Al}Y' \rightarrow \text{Fe}Y' + \text{Al}^{\cdots} \qquad \text{.. .. ..} \qquad (3)$$

This behaviour resulted in a rapid fading of the titration end-point.

The above difficulties were eventually overcome by boiling the aluminium solution with an excess of EDTA at pH 6. The quantitative formation of the aluminium complex was then in accordance with the reaction in equation (2). It was observed that unless the solution was cooled before the titration with ferric chloride the end-point was always poor, indicating that elevated temperatures favoured a reaction of the type illustrated in equation (3).

The following optimum conditions for the aluminium titration were eventually developed. To the aluminium, which was dissolved in dilute hydrochloric acid, a standard EDTA solution prepared from the disodium salt was added in about 10 per cent. excess and the pH was adjusted with diluted ammonium hydroxide (1 + 4) until the solution was just alkaline to methyl red. The solution was then boiled for 2 minutes, cooled, 3 g of ammonium acetate were added and the pH was adjusted to 6·5 with ammonium hydroxide, against a pH meter. About 0·2 g of salicylic acid was then added and the solution was titrated with a standard ferric chloride solution until the brown iron salicylate colour persisted. For solutions containing less than 30 mg of aluminium, a 0·02 *M* EDTA solution was used with 0·02 *M* ferric chloride for titrating the excess of EDTA; for solutions containing more than 30 mg of aluminium, 0·1 *M* reagents were used.

By the procedure outlined above, the results given in Table I were found, showing that the method is capable of determining amounts of aluminium up to 60 mg with an accuracy of better than 1 per cent.

TABLE I

RESULTS FOR ALUMINIUM BY THE EDTA TITRATION PROCEDURE

Aluminium taken, mg	Aluminium found, mg	Error, %
2·5	2·52	+0·8
5·0	4·96	−0·8
15·0	14·89	−0·7
30·0	29·95	−0·2
60·0	59·80	−0·4

After the separation of aluminium from other elements by precipitating aluminium benzoate according to the technique reported by Wilson,[5] solution of this precipitate in hydrochloric acid would result in the presence of benzoate ions in solution during the titration procedure. Experiments showed, however, that no difficulties occurred owing to the presence of these ions. The aluminium benzoate precipitate was washed from the filter-paper with water and collected in a 250-ml squat beaker. A 20-ml portion of hot diluted hydrochloric acid (1 + 1) was next added to the original precipitation beaker and then it was poured over the filter-paper to dissolve any traces of the aluminium precipitate, the paper being finally washed with water to give a total volume of solution of about 100 ml. The acid and washings were collected in the 250-ml squat beaker with the benzoate precipitate. The beaker and contents were warmed to ensure the complete solution of the aluminium benzoate precipitate and the titration was completed as for a pure aluminium solution. The results shown in Table II were found by this procedure.

TABLE II

RESULTS FOR ALUMINIUM AFTER PRECIPITATION AS ALUMINIUM BENZOATE

Aluminium taken, mg	Aluminium found, mg	Error, %
2·5	2·48	−0·8
5·0	5·00	nil
15·0	14·88	−0·7
30·0	30·09	+0·3
60·0	59·64	−0·7

APPLICATIONS OF THE ALUMINIUM TITRATION TO NON-FERROUS ALLOYS

MAGNESIUM-BASE ALLOYS—

The following method proved suitable for the rapid determination of the aluminium content of magnesium alloys complying with the specifications DTD 136A and DTD 289.

REAGENTS—

All reagents should be of the highest purity and distilled water must be used throughout.

Ammonium benzoate, 10 per cent. solution—Dissolve 10 g of solid reagent in 100 ml of water with warming. Cool and filter if necessary.

Ammonium acetate, 10 per cent. solution—Dissolve 10 g of solid reagent in water and dilute to 100 ml.

Ammonium benzoate wash solution—Dissolve 10 g of ammonium benzoate in water with warming. Then add 20 ml of glacial acetic acid and dilute to 1 litre with water.

Standard iron solution, 0·1 M—Dissolve 5·585 g of Specpure iron in 20 ml of hydrochloric acid, sp.gr. 1·16, and then oxidise with a few millilitres of nitric acid, sp.gr. 1·42. Dilute the solution to 1 litre with water.

Ethylenediaminetetra-acetic acid solution, 0·1 M—Dissolve 37·23 g of the disodium salt of ethylenediaminetetra-acetic acid in water and dilute to 1 litre. Determine the exact molarity of this solution by the following standardisation procedure. Transfer 20 ml of the standard 0·1 *M* iron solution to a 150-ml beaker and then add 25 ml of the EDTA solution. Add diluted ammonium hydroxide (1 + 4) to adjust the pH to a value of 6 against a pH meter and then boil the solution for 2 minutes. After cooling the solution to room temperature, add 3 g of ammonium acetate and re-adjust the pH to 6, if necessary. Transfer the solution to a 250-ml flask, add 0·2 g of salicylic acid and titrate with the standard iron solution until the colour of the solution changes from yellow to brown. Then—

$$\text{Molarity of EDTA} = \frac{(20 + \text{iron titration in ml}) \times 0{\cdot}1}{25}$$

PROCEDURE—

Add a few millilitres of water to 0·1 g of alloy in a 125-ml conical beaker and then slowly add 10 ml of hydrochloric acid, sp.gr. 1·16. After the initial violent attack, boil the solution for a few minutes. Transfer the sample solution to a 400-ml squat beaker, rinsing the conical beaker with water so as to give a total volume of about 250 ml. Dissolve 1 g of ammonium chloride in this solution. Then add 1 ml of 90 per cent. thioglycollic acid, 20 ml of 10 per cent. ammonium acetate solution and 20 ml of 10 per cent. ammonium benzoate solution. Heat the solution to 80° C, add sufficient hydrochloric acid to dissolve any precipitated aluminium benzoate and then slowly add diluted ammonium hydroxide (1 + 1) until a faint permanent precipitate appears. Boil the solution for 2 minutes and then add diluted ammonium hydroxide (1 + 4) to give a pH of 4 as shown by universal indicator papers. Boil the solution for a further 2 minutes and leave it warm for about 30 minutes to digest before filtering it through a Whatman No. 541 filter-paper; wash the precipitate well with the hot benzoate wash solution. Remove the precipitate from the paper, dissolve it in 20 ml of hot diluted hydrochloric acid (1 + 1) and complete the titration as above.

The results for typical magnesium-alloy samples, which were analysed in duplicate, are shown in Table III. Good agreement was found between the aluminium contents by the above method and those by standard gravimetric procedures.

TABLE III

RESULTS FOR THE DETERMINATION OF ALUMINIUM IN MAGNESIUM-BASE ALLOYS

	Composition							
Type of alloy	Cu, %	Fe, %	Si, %	Mn, %	Zn, %	Ni, %	Al, %	Aluminium determined by EDTA method, %
DTD 136A ..	0·09	0·018	0·13	0·22	0·42	0·007	9·4	9·41, 9·32
DTD 289 ..	0·09	0·011	0·05	0·217	1·19	0·007	8·25	8·15, 8·16

ZINC-BASE ALLOYS—

As Mazak alloys have aluminium contents in the region of about 4 per cent., 0·2-g samples were taken for the analysis of standard Mazak alloys. After solution of the sample in 10 ml of hydrochloric acid, the precipitation and separation of the aluminium benzoate from the other sample constituents was carried out according to the above method for magnesium-base alloys. Table IV shows that there was fairly good agreement between the results by the above volumetric method and those by the British Standard chemical procedure. In general, the volumetric aluminium values tended to be slightly higher than the chemical results. In spite of this small discrepancy the volumetric method is completed in a fraction of the time needed for the chemical method and can, therefore, have some advantages for the routine analysis of this type of alloy.

TABLE IV

RESULTS FOR THE DETERMINATION OF ALUMINIUM IN MAZAK ALLOYS

Sample number	Aluminium found	
	Chemically according to method of B.S. 1005: 1942, %	Volumetrically by EDTA method, %
A1	2·97	3·05
A2	3·50	3·55
A3	4·05	4·06
A4	4·56	4·62
A5	5·20	5·30

COPPER-BASE ALLOYS—

In the analysis of copper-base alloys the aluminium benzoate was precipitated and removed from other sample constituents by the procedure previously recommended by Milner and Townend.[1] After solution of this precipitate in 20 ml of hot diluted hydrochloric acid (1 + 1), the aluminium content was determined by the EDTA titration procedure. Typical results for the determination of aluminium in different types of copper-base alloys are in Table V.

TABLE V

RESULTS FOR THE DETERMINATION OF ALUMINIUM IN VARIOUS COPPER-BASE ALLOYS

Type of alloy	Composition								Aluminium found by EDTA titration, %
	Cu, %	Pb, %	Fe, %	Mn, %	Sn, %	Ni, %	Zn, %	Al, %	
Aluminium bronze ..	80·70	—	4·70	0·10	—	5·10	—	9·20	9·33
Propeller metal ..	55·94	<0·02	1·06	0·25	1·30	0·02	remainder	0·25	0·26
B.C.S. brass "B" ..	58·8	0·78	0·91	1·03	1·75	1·01	33·9	1·62	1·62
Manganese brass ..	57·65	1·09	0·19	0·81	1·18	0·03	remainder	<0·005*	nil

* By spectrographic analysis.

Thanks are due to Messrs. A. S. Nickelson and A. Bacon for supplying several analysed samples and also to the Director, A.E.R.E., for permission to publish.

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A Volumetric Method for the Rapid Assay of Palladium Jewellery Alloys

By R. H. ATKINSON

A volumetric method suitable for the assay of palladium has been developed. It is based on the precipitation of palladium as palladous iodide under appropriate conditions, with the precipitate as its own indicator. It has been shown that the presence of 5 per cent. of nickel, iridium, platinum, rhodium, tungsten, molybdenum, copper and tin do not interfere within 5 parts in 1000; interference by gold and silver can be obviated by suitable modifications of procedure. In the analysis of a palladium - ruthenium alloy, 15-mg samples are dissolved in the minimum amount of concentrated aqua regia and the resulting solutions are titrated with 0·01 *N* potassium iodide, after adding hydrochloric acid and ferrous sulphate, the latter to prevent excess of aqua regia from reacting with the potassium iodide. The titration is continued until there is no cloud when a drop of the iodide solution is added; owing to the slowness with which palladous iodide settles, it is necessary to centrifuge a portion of the alloy solution before adding the test drop.

WITH the increasing use of palladium for jewellery and industrial alloys a need has arisen for a simple, rapid and accurate method for determining it in its alloys. This is especially true in countries where assays are required in connection with the hallmarking of jewellery. Scott[1] describes a gravimetric method in which the palladium is precipitated as the iodide, which is converted to the metal before weighing. It has been found that the palladium content of a solution of palladium chloride can be determined by titration with a standard solution of potassium iodide, in much the same way as a solution of silver nitrate is titrated with a standard solution of sodium chloride in the classical Gay-Lussac method for silver. In both determinations the titration is continued until a cloud fails to form when a drop of the titrant is added, the only difference being that the settling of the palladous iodide has to be assisted by centrifuging before adding the test drop. In this way a dilute solution of palladium chloride can be titrated with 0·01 *N* potassium iodide with a reproducibility of ±0·05 ml.

REAGENTS—

The precious metals used in the investigation, *i.e.*, palladium, platinum, rhodium, ruthenium, iridium, gold and silver, were purchased from Baker and Co., U.S.A., as pure metals. Base metals used were commercially pure and chemicals and acids were of recognised analytical grade.

Standard palladium solution—To make a standard solution of palladium (containing 1 g of metal, as chloride, per litre) dissolve the pure metal in aqua regia and remove excess of nitric acid by evaporating several times with hydrochloric acid and finally making up to volume with *N* hydrochloric acid.

Potassium iodide solution, 0·01 N—Dissolve 1·8603 g of potassium iodide (dried by heating at 120° C for 2 hours) in 1 litre of distilled water that had been de-oxygenated by bubbling an inert gas (argon was used but pure nitrogen would do equally well) through it; also, treat the solution with inert gas at the end of each day after use; keep it in a dark bottle with a tightly fitting stopper in a dark cupboard. When prepared carefully as described the solution will be 0·01 *N*, but it is best to standardise it against either pure palladium or a standard solution of palladium chloride containing 1 g of palladium per litre. The iodide solution should be re-standardised each week because it loses strength slowly. In early tests sodium iodide (U.S.P.) was used for the titrations, but it was found to be too hygroscopic for use as a standard.

Ferrous sulphate solution—Dissolve 20 g of ferrous sulphate crystals, $FeSO_4.7H_2O$, in 100 ml of distilled water acidified with a few drops of concentrated sulphuric acid.

NOTE—If a solution of pure palladium chloride is used for standardising the potassium iodide solution, the ferrous sulphate solution should be weaker (say, 15 per cent. w/v), because with the 20 per cent. solution low titres, accompanied by reduction of some palladium to metal, may be encountered.

SELECTIVITY OF IODIDE TITRATION—

The effect of other metals on the titration was determined by adding 5 per cent. (0·5 mg) of the metal, or metals, usually as chlorides, to 10 ml (equivalent to 10 mg of palladium) of the palladium chloride solution, followed by 5 ml of concentrated hydrochloric acid and 15 ml of 15 per cent. ferrous sulphate solution, and then titrating with the standard solution of potassium iodide. Tungsten and molybdenum were added as sodium tungstate and molybdate, respectively. After the addition of the ferrous sulphate to the test solution containing gold, the mixture was allowed to stand at room temperature (21° C) for 1 hour before titration. In the absence of ferrous sulphate, gold will increase the titre. In presence of silver, which interferes with the titration even when ferrous sulphate is present, the test was modified as follows. Palladium (0·100 g) was dissolved in warm dilute aqua regia, the minimum amount of nitric acid being used; after adding 0·005 g of silver dissolved in the minimum amount of warm dilute nitric acid, the combined solution was evaporated to dryness at 105° C. The residue was treated with about 5 ml of distilled water, then made up to exactly 100 ml and left to settle in a dark cupboard for 24 hours; the pH of the solution was 1·6. Aliquot portions of the clear solution were taken for titration. Typical results for the titration of solutions of palladium chloride with and without the addition of other metals are recorded in Table I. It will be seen that 5 per cent. of nickel, iridium, platinum, rhodium, tungsten, molybdenum, copper and tin do not interfere with the iodide titration within the claimed limit of accuracy and that interference by gold and silver can be obviated by suitable modifications of procedure.

TABLE I

EFFECT OF OTHER METALS ON IODIDE TITRATION OF PALLADIUM CHLORIDE

10 mg of palladium taken

Added metal	Volume of 0·01 *N* potassium iodide required, ml
None	18·82, 18·80, 18·85, 18·80, 18·88
Ni (0·8 mg) + Ir (0·5 mg) as chlorides*	18·80, 18·90
Pt^{IV} (0·5 mg) + Rh^{III} (0·5 mg) as chlorides	18·85, 18·85
W (0·5 mg) as H_2WO_4 Mo (0·5 mg) as H_2MoO_4	18·80, 18·80
Cu^{II} (0·5 mg) + Sn^{IV} (0·5 mg) as chlorides†	18·82, 18·85
Ag (0·5 mg) as nitrate‡	18·85, 18·82
Au (0·5 mg) as $HAuCl_4$§	18·83

* Chlorides were made by dissolving nickel - iridium alloy in aqua regia and evaporating just to dryness.

† Acidity was increased in these tests (10 ml of concentrated hydrochloric acid instead of 5 ml).

‡ Silver chloride was separated before titration.

§ Solution allowed to stand for 1 hour before titration. In the absence of ferrous sulphate the titre was 19·38 ml.

ASSAY METHOD

The procedure finally developed for the assay of palladium - ruthenium (95·5 + 4·5 per cent.), a typical jewellery alloy, was as follows.

Weigh a piece of the alloy (about 15 mg) accurately on an assay balance and place it in a 100-ml round-bottom Pyrex flask, and add 0·20 ml of concentrated hydrochloric acid and 0·04 ml of concentrated nitric acid from burettes or dropping tubes. Dissolve the alloy by heating the flask in a water-bath at about 85° C. If desired, a small funnel may be placed in the neck of the flask to catch spray. After the metal has dissolved (allow 2 minutes), blow the brown fumes out of the flask with a current of air, add 5 ml of concentrated hydrochloric acid and 15 ml of ferrous sulphate solution, and titrate with 0·01 *N* potassium iodide. Run in slowly about 0·5 ml less than the expected amount of iodide, keeping the contents well stirred. Place the stopper in the flask, shake it vigorously for 1 minute, then transfer about 5 ml of the solution to a centrifuge tube and centrifuge it for 15 seconds. Add 1 drop of the iodide solution to the clear solution in the tube and judge the intensity of the cloud of palladous iodide. With experience it is possible to decide how much more iodide is required.

Return the contents of the tube to the flask and add more potassium iodide from the burette. After shaking the flask for 5 seconds, remove a portion, centrifuge it and test it as before. Continue the titration until the addition of the test drop fails to give a recognisable cloud.

Standardise the solution of potassium iodide against pure palladium, which is dissolved and prepared for titration exactly as described for the alloy.

NOTES—1. In order to facilitate dissolution, the metals should be in the form of thin foil, filings or scrapings.

2. It is important to avoid an unnecessary excess of aqua regia because the amount of ferrous sulphate (3 g) used in each assay is only equivalent to little more than 0·1 ml of concentrated nitric acid.

3. The ferrous sulphate must be added after the hydrochloric acid because the ferrous sulphate is capable of reducing palladium chloride to metal when the acidity is low.

4. Vigorous shaking is necessary to cause coagulation of the palladous iodide so that the solution will be clear after centrifuging. For centrifuging a hand centrifuge was used; this was operated at a rate that gave a velocity of about 8500 feet per minute at the solution level.

5. A suitable background is very helpful in detecting the end-point. A uniformly dull or overcast sky makes a suitable background against which to observe the thin "clouds" formed near the end-point. If the sky is bright, a small sheet of tracing paper (11 inches × 8 inches) attached to a window pane with Scotch tape can be used as background.

Results of the assay of the palladium - ruthenium alloy by the present volumetric method are compared, see Table II, with the results for duplicate gravimetric assays in which the palladium was separated and determined as the dimethylglyoxime complex.

TABLE II

COMPARISON OF RESULTS OF GRAVIMETRIC AND VOLUMETRIC ASSAYS OF RUTHENIUM - PALLADIUM

Weight of alloy, mg	Volume of potassium iodide, ml	Palladium content, %
15·54	27·95	95·6
15·77	28·45	95·9
15·44	27·80	95·7
54·1	gravimetric assay	95·8
53·0	„	95·9

Stronger palladium solutions can be titrated with 0·1 *N* potassium iodide; the end-point is sharper but the improvement is not sufficient to offset the other advantages of working with 0·01 *N* solutions, *e.g.*, smaller samples and a smaller excess of aqua regia are required.

In spite of the time spent in centrifuging and testing for the end-point, the present method is rapid compared with any gravimetric method for the determination of palladium. Moreover, the accuracy claimed for the method in its present stage of development, namely, 5 parts per thousand, is thought to be on the conservative side and there does not appear to be any reason why higher accuracy should not be attained when assaying a standard jewellery palladium alloy.

The author wishes to thank Mr. T. Walsh of Baker and Co., for placing an assay balance at his disposal, also colleagues of the International Nickel Company and the Mond Nickel Company, especially Dr. R. N. Rhoda and Mr. R. G. Lomell of the former company, for help in various ways.

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BAYONNE
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An Improved Method for the Analysis of Gaseous Mixtures on the Micro Scale

By G. H. BUSH and R. J. LONERAGAN

The various micro methods of gas analysis are reviewed briefly, and a modification of the apparatus and method used by Sutton, but in which dry reagents are used, is described. The method, in which a simply constructed capillary burette is used at constant pressure, enables a rapid analysis of a mixed gas to be carried out on a volume of about 0·1 ml with a precision comparable to that attained on the macro scale.

THE technique to be described was developed for the identification of quantities of mixed gases, of the order of 0·5 ml at S.T.P., evolved from a sample being induction-heated under very low pressure. The method of handling the small volumes of gas and a description of the apparatus and procedure used for the quantitative analysis will be given. There is a brief review of other micro methods of analysis that have been proposed. The apparatus and technique have been found to be adaptable, and their use is not restricted to the analysis of the mixture to be described. By a suitable choice of reagents and modifications of technique, the apparatus can be used for the analysis of many other combinations of gases.

Transport of the gas was facilitated by the use of a bottle of the type shown in Fig. 1. This was an ordinary 1-ounce wide-mouthed screw-capped bottle, whose cap was fitted with a rubber grommet of such a size that it firmly gripped the test tube. This cap was fitted on to the tube before the gas was collected, and the tube containing the gas sample was placed in the bottle under mercury.

MICRO METHODS OF ANALYSIS—

Several methods have been proposed for the analysis of small volumes of gas. The constant-volume principle necessitates working at reduced pressures to attain the accuracy required, and this leads to errors due to adsorption of gas on the walls of the apparatus. At low pressures the efficiency of absorbents, particularly desiccants, is seriously impaired and errors are introduced owing to the relatively high vapour pressure of some reagents. The purely physical method described by Ransley[1] obviates the errors due to chemical absorbents by avoiding the use of these reagents. This necessarily restricts the range of usefulness of the method, as gases with widely differing chemical properties, but with similar physical properties, may not be distinguished. In addition, the apparatus itself is complex, requiring Pirani gauges, palladium tubes, liquid air, and so on.

The constant-pressure principle applied on the micro scale results in simpler and smaller apparatus. The glycerol bubble method of Price and Woods,[2] devised for the analysis of gas bubbles occurring in glass, requires, apart from a microscope, apparatus of very simple design. However, the accuracy of this method was not considered sufficient for the work that was being undertaken. Its main disadvantages are the solubility of the sample in glycerol, the instability of some reagents in glycerol, the fact that the bubbles are not always spherical and, lastly, the difficulty of determining hydrogen and methane.

The most promising technique appeared to be one in which a capillary burette is used to measure the gas, the most suitable confining liquid being mercury. In the design described by Blacet *et al.*,[3,4,5] the capillary burette is vertical; this leads to the necessity for robust seals at the lower extremity and also requires careful setting in order that the pressure on the gas may be kept constant. Swearingen, Gerbes and Ellis[6] modified the earlier designs by the introduction of a horizontal burette, and Sutton[7] described an apparatus in which the burette and reaction chamber were in one piece. This last apparatus appeared to have all the necessary simplicity of design and manipulation and, in addition, the accuracy attainable was claimed to be of the same order as in macro-analysis.

Working with this apparatus it was found that wet reagents absorbed on porous beads, as proposed by Sutton, produced erratic results, and many an analysis could not be completed owing to contamination of the mercury with reagent, although the use of a standard wet reagent, *e.g.*, cuprous sulphate - 2-naphthol in sulphuric acid for carbon monoxide, for the purpose of checking any particular constituent of a gas, as distinct from a complete analysis, gave satisfactory confirmatory results.

On modifying the apparatus slightly, using dry reagents throughout, and keeping the mercury in the trough clean, it was found that the accuracy required was easily attainable and that the steel guide tube described by Sutton was unnecessary. Clearer observation of the reagent beads was possible, and with a little practice it was found that fewer errors were attributable to the operations carried out in the reaction chamber.

It was decided that, if the number of reagents required was reduced to the minimum, the method would be more satisfactory for routine work, and the reagents mentioned below were therefore chosen.

REAGENTS—

Anhydrone—This reagent was regarded as superior to phosphorus pentoxide for the purpose of removing water, as no particular care in handling is required, only water vapour is absorbed (phosphorus pentoxide absorbs ammonia) and the surface of the reagent remains dry.

Soda-asbestos—A fused bead of this reagent containing approximately 80 per cent. of sodium hydroxide was preferred to one of fused sodium or potassium hydroxide for the absorption of carbon dioxide. Absorption took place more rapidly and a bead could be left in the air for longer periods without the objectionable liquid film forming on the surface.

Phosphorus—It was found that, unless a smooth bead of reagent was used, small volumes of air were frequently admitted and equal amounts of gas mixture were removed with the bead. This was a serious difficulty when small pieces of phosphorus of irregular shape held in a platinum loop were used to remove oxygen. In addition, it was confirmed that, at room temperature, phosphorus was passive in a concentration of oxygen above about 30 per cent., but that activity could be restored by gently warming it. A reagent holder has been devised to enable a smooth bead to be produced and, at the same time, to permit gentle warming of the bead when it is in position in the reaction chamber.

TABLE I

SOLID REAGENTS

Reagent	Gas absorbed
Anhydrone	$\mathbf{H_2O}$
Soda-asbestos..	$\mathbf{CO_2}$, HCl, SO_2, H_2S, $\mathbf{NO_2}$
Silver oxide	$\mathbf{CO}$
Cupric oxide - potassium hydroxide at 300° to 400° C ..	$\mathbf{H_2}$, CO
Phosphorus pentoxide	H_2O, $\mathbf{NH_3}$
Yellow phosphorus	$\mathbf{O_2}$
Cuprous chloride - potassium hydroxide	$\mathbf{C_2H_2}$
Manganese dioxide - cupric oxide	$\mathbf{CO}$, H_2, CH_4

Oxygen—This gas is used for the determination of combustible gases, *e.g.*, hydrogen, carbon monoxide and methane, and is purified by being passed through a refractory tube at approximately 1000° C, wash-bottles of chromic acid - sulphuric acid mixture and a tube containing glass-wool, granular soda-asbestos and anhydrone, in that order. Its purity is determined either by a standard macro technique or by exploding it with hydrogen, as the reaction between heated phosphorus and relatively pure oxygen is so vigorous that any residual gas is dispersed and cannot be measured readily.

Hydrogen—This can be used conveniently in the determination of nitrous oxide by the use of a hot wire to effect the reaction, or as an alternative reagent in place of phosphorus for the determination of residual oxygen. It also provides a satisfactory method for the determination of the purity of the oxygen used in the analysis of mixtures of combustible gases. A suitable hydrogen purification train consists of (*a*) platinised asbestos at 800° C, (*b*) soda-lime, (*c*) anhydrone and (*d*) a cold trap immersed in liquid nitrogen or solid carbon dioxide - acetone mixture, the connecting tubing from the cold trap being kept as short as possible.

It is convenient to determine the purity of hydrogen and oxygen at the same time by alternately exploding a mixture with an excess of one gas and then the other, measuring the volume at each stage in terms of length of capillary tube and determining the purity

Fig. 1. Gas transport bottle

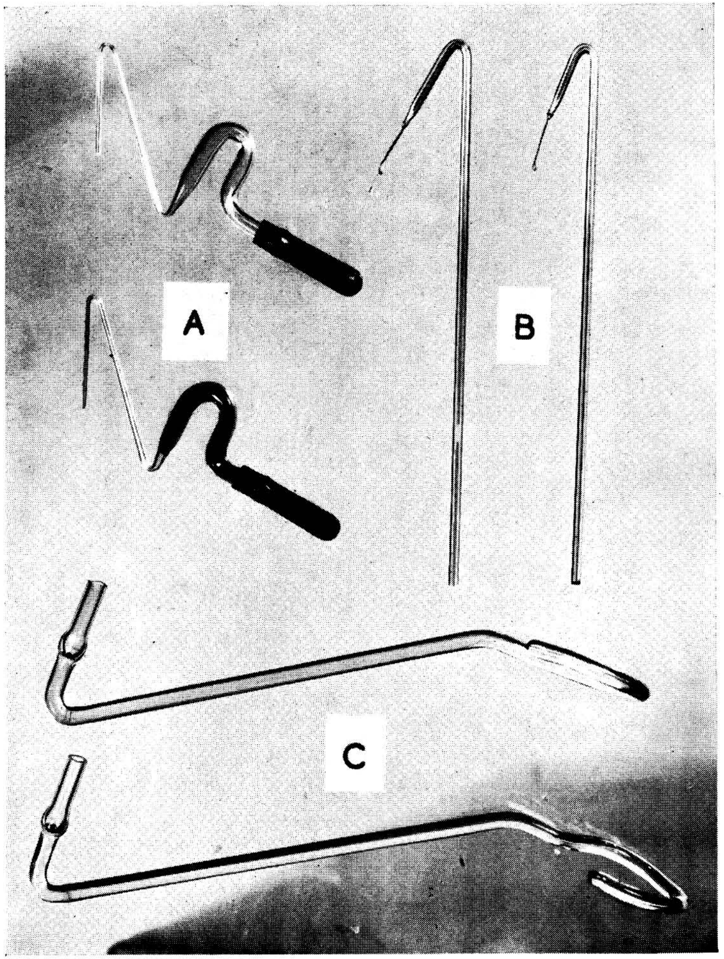

Fig. 3. A, gas pipettes; B, reagent holders; C, storage reservoirs for hygroscopic reagents

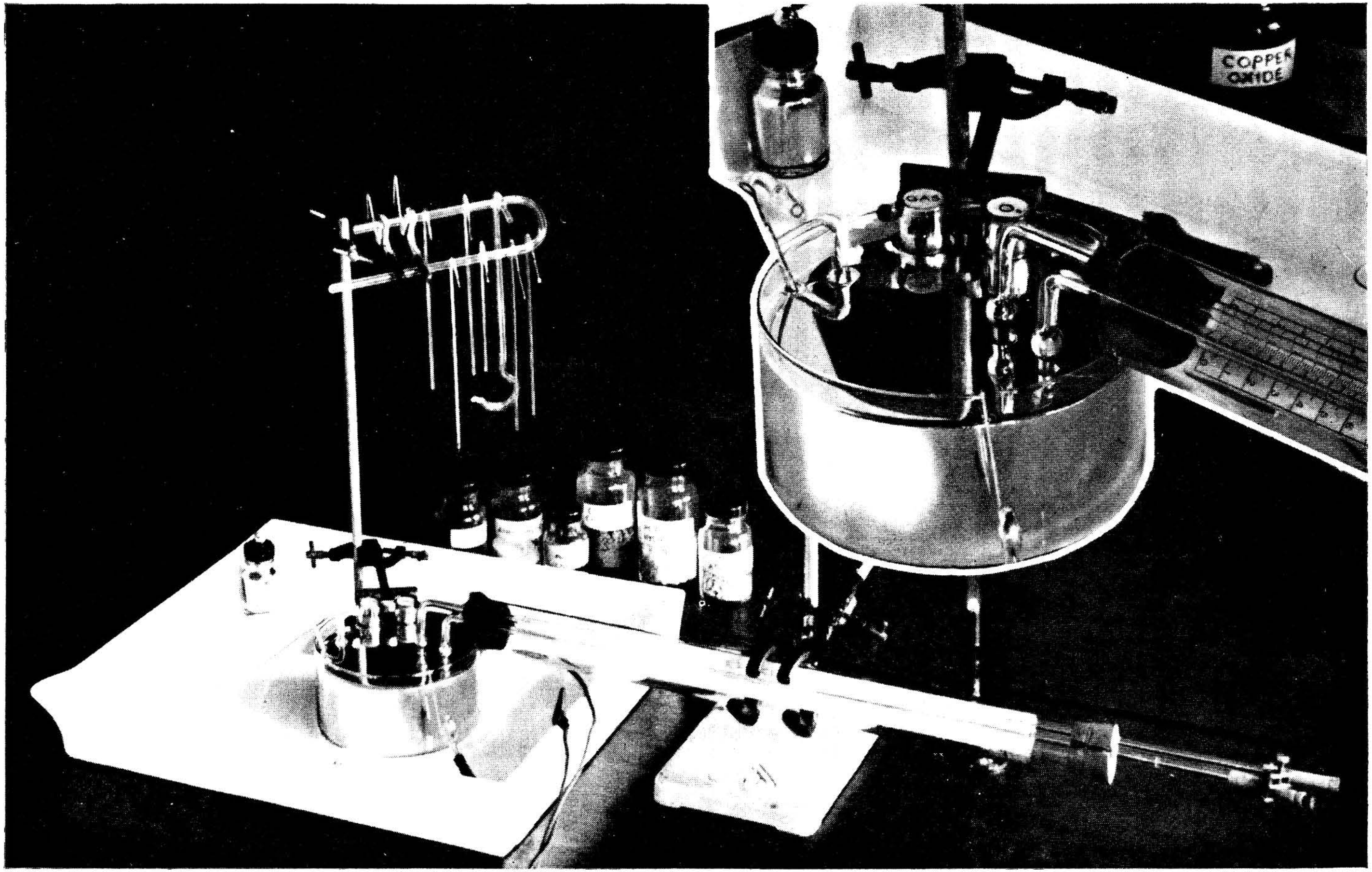

Fig. 2. General arrangement of apparatus

of each gas from the contractions observed. For example, beginning with approximately 20 cm of hydrogen and 5 cm of oxygen, explosion leaves about 10 cm of hydrogen to which 10 cm of oxygen are added; on explosion this leaves about 5 cm of oxygen to which 20 cm of hydrogen are added, and the cycle is repeated as often as desired. In this way it is possible to explode comparatively large volumes in the micro apparatus.

With these reagents and the use of a hot wire, it was found possible to analyse mixtures of carbon dioxide, hydrogen, carbon monoxide, oxygen, methane and nitrogen by the method to be described. Reagents suitable for use in this method are listed in Table I. The gases for which each is most generally useful are printed in bold type.

APPARATUS

Sutton specified a 0·5-mm bore tube for the gas burette but, although the choice of the bore would be governed by the volume of the samples normally encountered, the scale on which it is most simple to operate is one with a sample volume of 0·1 to 0·2 ml and a tube of 1-mm bore. The dimensions to be given refer to apparatus for work on this scale. The general arrangement of the apparatus that has been constructed is shown in Fig. 2.

Gas burettes—The apparatus consists essentially of a horizontal thick-walled capillary tube of uniform bore, approximately 65 cm long, closed at one end by a rubber cap, which can conveniently be made from a short piece of flexible rubber tubing and a small rubber bung. The other end of the capillary is bent at right angles about 2·5 cm from the tip and fused to a short piece of 4-mm bore tubing with a small bulb blown at the joint to form the reaction chamber. The length of the vertical portion from the bend to the tip should be about 5·5 to 6·0 cm. The straight portion of the tube, together with a second tube of similar dimensions, rests on a white-glass scale marked in millimetres and supported on corks. This arrangement enables the volume of the gas to be determined accurately and eliminates completely the parallax error inherent in Sutton's design. The tubes and white-glass scale are enclosed in a glass jacket, 4 cm in diameter and approximately 50 cm long, the ends of which are sealed by two rubber bungs through which pass the two burette tubes. This assembly is supported horizontally so that the open ends of the gas burettes are immersed to a depth of about 1 cm in a trough of mercury, which should be about 15 cm in diameter and at least 5 cm deep.

Gas holders—The gas samples to be analysed and the oxygen and other gases used in the analysis are best kept in small shallow gas-holders supported in the trough of mercury mentioned above. These gas holders may conveniently be small squat beakers or shortened specimen or test tubes, but should not exceed about 2·5 cm in height.

Gas pipettes—The gases are handled by means of gas pipettes illustrated in Fig. 3, A. The body of the pipette is of 4 to 5-mm tubing and the capillary tip is drawn down from this, after thickening in a flame, to 0·2 to 0·3-mm bore and of 1 mm outside diameter. The vertical part of the capillary tip should be approximately 3 cm long.

Reagent holders—The reagent holders (Fig. 3, B) consist of short pieces of 0·020-inch diameter platinum wire sealed into 3-mm diameter glass rods or capillary tubing. The longer side is between 15 and 20 cm long and the length from the tip of the platinum loop to the bend is 4 cm. The most convenient angle for this bend and that in the gas pipette has been found to be in the region of 20°. If tubing is used, care should be taken to ensure that the glass-to-metal seal is gas-tight.

Sutton's liquid reagent reservoirs, shown in a slightly modified form in Fig. 3, C, although not used for their original purpose, serve admirably for the storage of hygroscopic reagents.

The reagent holder for yellow phosphorus and the hot-wire holder (Fig. 4) are made to the same over-all dimensions, but in these the wires are sealed through the 2-mm bore tubing, which is then filled with mercury in order to make contact with the wire inside the tube. The wire is coiled and bent back as shown in the diagram, the height of the coil from the tip of the glass being kept as small as possible. Suitable wire for the phosphorus holder is 0·0124-inch diameter (30 S.W.G.) nichrome, and 0·005-inch diameter platinum should be used for the hot wire. Contact with the mercury at the open end of the tube is made with a short twist of nickel or iron wire sealed in with beeswax.

PREPARATION OF REAGENT BEADS—

As far as possible reagent beads should be prepared by fusion to the wire over a micro-burner. This method has the advantage of producing a smooth bead that adheres well to the holder. With yellow phosphorus this method of preparation is out of the question, and the procedure to be described should be adopted.

Anhydrone—As purchased, anhydrone is a light, granular form of anhydrous magnesium perchlorate, which, on exposure to the air, rapidly absorbs water to form, first, the trihydrate, $Mg(ClO_4)_2.3H_2O$, which is still very hygroscopic. The anhydrous compound decomposes on heating, but the trihydrate dissolves in its own water of crystallisation at about 120° C. Use is made of this fact in the preparation of the reagent bead.

Place a little anhydrone on a glazed tile or watch-glass, strongly heat the platinum loop of one of the reagent holders in a flame and, while it is still hot, touch a few grains of the solid lightly to make them adhere. Heat gently, a few inches above a small flame, just sufficiently to cause the particles to coalesce to form a smooth bead. As soon as it solidifies, keep the bead under mercury as described earlier. By heating under vacuum it is possible to dehydrate the magnesium perchlorate completely, but no advantage is gained by this treatment.

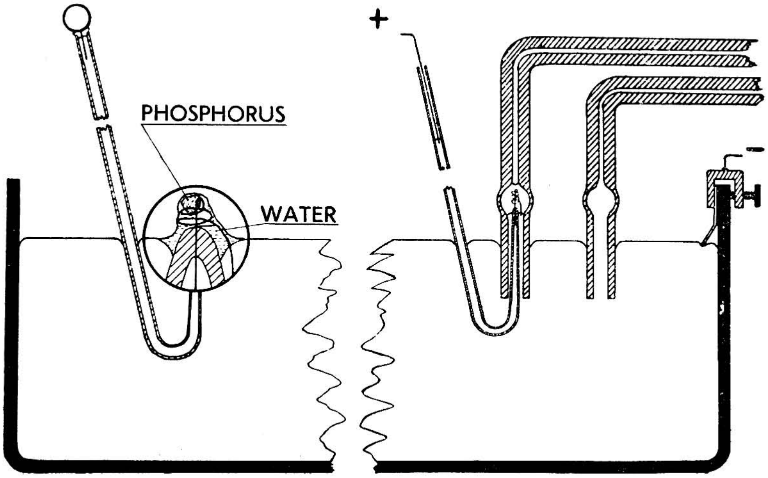

Fig. 4. (*a*) Preparation of phosphorus bead, (*b*) technique of gas ignition

Soda-asbestos—The method of preparation of a soda-asbestos bead is similar to that described for anhydrone, except that a higher temperature is required.

Use the product containing about 80 per cent. of sodium hydroxide of 14 to 20 mesh and heat just sufficiently to form a smooth bead; prolonged heating in a gas flame only serves to convert most of the sodium hydroxide to carbonate. Inspect the bead carefully when it is cold as there is a tendency for cavities to form on cooling. Keep the reagent under mercury until it is required for use and activate its surface by breathing gently on it immediately before use. Frequently a new bead will not absorb carbon dioxide from a high concentration until it has been activated in this way.

Yellow phosphorus—Connect the mercury-filled holder fitted with the nichrome coil to a variable low-tension supply, and complete the circuit through the mercury bath. This circuit can, with advantage, be controlled by a foot-operated switch. Increase the current gradually from a low value until a drop of water placed on the coil becomes warm but does not evaporate rapidly. Interrupt the current and place about a cubic millimetre of yellow phosphorus centrally on the coil, thoroughly moisten it with water and fuse it to the wire by closing the circuit again (see Fig. 4*a*). Dry the bead with acetone and store it under mercury.

Hot wire—Determine the temperature - current relationship for the fine platinum coil by making contact through the mercury in the bath and increasing the current from a low value. It will be found that a source of 6 to 8 volts will be required.

The method of using these heated reagent holders is the same as for the simple platinum loops, but care must be taken to ensure that the glass tip of the holder is projecting through the mercury or the current will be short circuited and no heating will occur. The technique of gas ignition is illustrated in Fig. 4*b*.

METHOD

SETTING UP THE GAS BURETTES—

Fill the two gas burettes with mercury by first filling the rubber cap and then pushing this carefully over the end of the capillary tube, taking care to avoid trapping any air. Normally this will only partly fill the tube. Complete the operation by rotating the tube until the open end is uppermost, squeeze the rubber cap to expel air from the capillary portion and then pour in mercury until the bulb and tube are completely full. With the thumb placed firmly over the end, rotate the tube through 180° so that the end of the tube is about 1 cm below the surface of the mercury, and adjust the height of the burette assembly if necessary. Inspect the whole length of the tube to ensure that it is free from air bubbles.

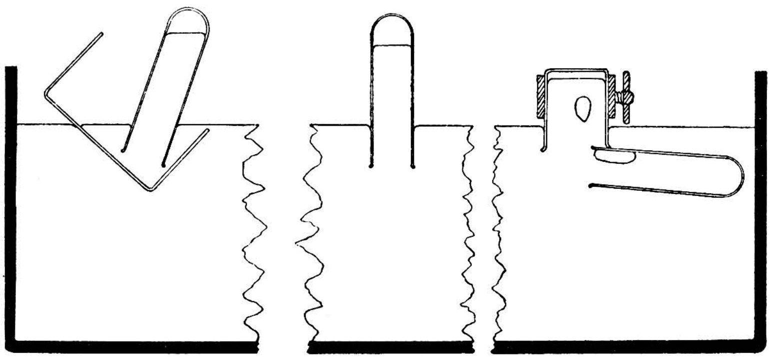

Fig. 5. Transfer of gas from collecting tube to gas-holder

Introduce a small volume of air, equivalent to about 25 cm of the capillary, into the rear tube by means of the gas pipette and draw it into the horizontal part of the tube. Measure and record the length of this column of air. Eliminate parallax by reading with one eye and observing the scale both directly and through the capillary tube. Tap the outer jacket gently to ensure that the rubber cap has reached equilibrium and to avoid errors due to uneven distribution of surface tension between the two menisci. Move the column along to the other end of the tube, re-measure the volume and adjust the angle of the tube until the length of the column is the same when measured at each end of the tube. This method of setting the tube has been found to be most satisfactory.

To correct for changes in atmospheric temperature and pressure, measure the length of this column of air at intervals during the analysis.

TRANSFER OF GAS SAMPLE TO HOLDER—

Transfer the gas sample from the tube in which it was collected to a mercury-filled gas holder in the mercury trough, by immersing the tube and its mercury reservoir in the large mercury trough, removing the small dish with the test tube still immersed and tilting the tube with its open end under the gas holder so that the bubble of gas rises into it. The sequence of operations is shown in Fig. 5.

PROCEDURE—

Carefully fill a gas pipette with mercury and withdraw a portion of the sample from the gas holder by first squeezing and then releasing the pressure on the rubber cap. Draw a small amount of mercury into the pipette to isolate the gas from the atmosphere in the event of the tip breaking surface during the next operation. Introduce the gas into the front gas burette by bringing the tip of the pipette, still immersed in the mercury, up to the top of the reaction bulb and ejecting the gas into it. If the gas be released with the tip of the pipette low in the reaction chamber, bubbles may adhere to the sides and escape measurement until they are dislodged at some later time by a reagent holder. These operations are illustrated in Fig. 6.

Measure the initial volume of the gas as described earlier and introduce reagents in turn on the reagent holders by inserting the tip into the open end of the tube and up into the bulb.

It will be found that, with the exception of the mercury-filled tubes, the holders will float in this position. Drive the gas back into the reaction chamber by the application of pressure on the rubber cap. After the reaction or absorption has taken place, withdraw the reagent bead through the surface of the mercury in the bulb and draw the gas back into the capillary burette for re-measurement. It is important that this sequence be followed or a small bubble of gas can be trapped behind the reagent bead and escape measurement. With an oxygen concentration in excess of 30 per cent., cold phosphorus will absorb very slowly and the period of absorption would be increased from about 3 minutes to an hour or more. However, if only part of the sample has been taken for analysis, absorption may be completed in a few seconds by warming the phosphorus by passing a current momentarily through the nichrome wire, as described above for the preparation of the bead. With high oxygen concentrations the reaction is accompanied by the emission of light and considerable heat and a film of phosphorus may be deposited on the walls of the reaction bulb. Then, although the determination of oxygen remains unaffected, it may be necessary to discard the remaining gas and to clean the tube. It has been found that a burette contaminated with phosphorus is readily cleaned by removing it from the air jacket and running through it warm concentrated nitric acid followed by distilled water, after which it is thoroughly dried.

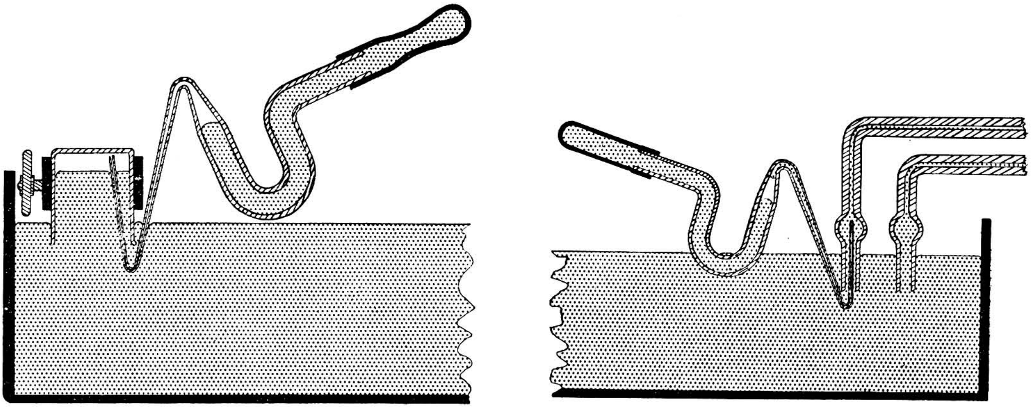

Fig. 6. Transfer of gas from gas holder to burette

SEQUENCE OF OPERATIONS FOR THE ANALYSIS OF GASEOUS MIXTURES

The gaseous mixtures that were analysed by this method consisted of carbon monoxide, hydrogen, carbon dioxide, methane, oxygen and nitrogen. The procedure adopted was as follows, absorption to constant volume being practised throughout.

PROCEDURE—

1. With a suitable volume of sample in the burette, remove water vapour with anhydrone and record the new volume in terms of length of tube, *a* cm. (Unless very carefully dried, the glass parts of the apparatus will desorb water to a previously dry gas, and unless the water is removed at this stage it will be determined as carbon dioxide.)

2. Remove carbon dioxide with activated soda-asbestos and re-measure the volume, *b*. It is advisable to use the desiccant bead at this stage to ensure that the gas being measured is dry.

3. Remove oxygen with yellow phosphorus warmed by means of the nichrome coil and record the volume, *c*. The subsequent procedure is as follows—

   (*i*) *With sufficient gas available for repeat determinations*—Discard the residual gas, clean the burette, and, with a fresh sample, dry the gas as in operation 1 and proceed from operation 4. The amounts of carbon dioxide and oxygen present, as determined earlier, should be allowed for in the calculation that follows. This procedure has been found to eliminate any error due to the possible contamination of the mercury surface and walls of the reaction chamber with caustic alkali from the soda-asbestos bead.

(*ii*) *With insufficient gas available for repeat determinations*—Remove the residual gas by means of the gas pipette to a clean, dry, storage reservoir whilst the burette is being cleaned. Then return the gas to the burette and re-measure, in case of loss, and continue the analysis.

4. Introduce an approximately equal volume (or an estimated excess) of purified oxygen whose purity has been determined either by the method mentioned under Reagents with purified hydrogen or by a standard macro technique. Dry the gas as before and re-measure to find the volume of oxygen added, d.

5. Adjust the current controller to raise the temperature of the fine platinum wire to about 1000° C. With the current switched off, introduce the wire into the gas in the reaction bulb, taking care that the glass tip of the holder is visible above the mercury surface. Pass the current until explosion occurs, and for about 30 seconds thereafter.

6. Dry the resultant gas mixture with an anhydrone bead as before. This should be carried out before drawing the gas into the capillary burette for measurement, to avoid wetting the tube. Determine the volume, e, as before and hence the contraction due to combustion, B.

7. Remove the carbon dioxide produced by the combustion of the carbon monoxide and methane, with a soda-asbestos bead following this with an anhydrone bead as before, and re-measure the volume of the gas, f. Then $e - f$ will give the volume of carbon dioxide produced, C.

8. The remaining gas consists of the excess of oxygen, nitrogen from the original gas and a little nitrogen from the oxygen added if this was not 100 per cent. pure. Remove the oxygen with the yellow phosphorus bead, applying a heating current to the coil. Record the volume remaining, g.

If it is desired to use hydrogen for the determination of residual oxygen, operation 8 is carried out as follows—

> 8. Introduce a volume of hydrogen slightly greater than $2f$ (or an estimated excess), dry the gas as before and re-measure it to find the volume of hydrogen added, h, explode and dry the resulting gas as described in operations 5 and 6, and re-measure it to determine the final volume, l, and hence the contraction at this stage, k. Then for the purpose of the following calculations—

$$g = l + \frac{2k}{3} - h.$$

It will be appreciated, on inspecting the equations given below, that the volume of oxygen consumed, A, and the volume of carbon dioxide produced, C, have a large effect on the results, and the greatest care should be exercised in the measurements involved in their determination.

CALCULATION OF RESULTS

All results are normally calculated on the dry gas but, if it is desired to know the water-vapour content of the gas sample, it is necessary to take the precaution of drying all the apparatus and mercury thoroughly before the gas is introduced into the apparatus. The above symbols are used in the following calculations. The purity of the oxygen is assumed to be m per cent.

$$\text{Carbon dioxide, per cent.} = \frac{a - b}{a} \times 100$$

$$\text{Oxygen, per cent.} = \frac{b - c}{a} \times 100$$

$$\text{Nitrogen, per cent.} = \left[g - \frac{(100 - m)d}{100}\right] \times \frac{100}{a}$$

Carbon monoxide, hydrogen and methane are calculated from three equations derived from the equations for the combustion of these gases.

$$\text{Hydrogen, per cent.} = \frac{B - A}{a} \times 100$$

$$\text{Carbon monoxide, per cent.} = \frac{4C + B - 3A}{3a} \times 100$$

$$\text{Methane, per cent.} = \frac{3A - B - C}{3a} \times 100$$

where A = volume of pure oxygen consumed

$$= \frac{md}{100} - (f - g)$$

B = contraction on combustion, and

C = volume of carbon dioxide produced.

Similar sets of equations may be obtained for mixtures of hydrogen and carbon monoxide with ethane, ethylene or acetylene and for hydrogen and methane with ethylene or acetylene. However, it is not possible to derive equations for mixtures containing more than one member of an homologous series, as such calculations lead to the evolution of parallel equations.

RESULTS

The following results have been determined on a gaseous mixture. The volume used in each determination was approximately 0·1 ml.

TABLE II

REPRODUCIBILITY OF RESULTS

Experiment	Carbon dioxide, %	Oxygen, %	Hydrogen, %	Carbon monoxide, %	Methane, %	Nitrogen, %
1	8·4	Nil	28·1	29·9	0·7	33·0
2	8·4	"	28·2	30·0	0·6	32·9
3	8·4	"	28·4	29·8	0·7	32·6
4	8·4	"	28·9	30·6	0·3	31·9
5	8·4	"	28·6	29·7	0·5	32·9
6	8·4	"	28·8	29·6	0·4	32·9
7	8·3	"	28·0	30·5	0·3	32·8
8	8·5	"	27·9	29·9	0·4	33·2
9	8·4	"	27·9	29·9	0·8	32·9
10	8·4	"	28·5	29·6	0·8	32·6
Mean	8·4	Nil	28·3	30·0	0·6	32·8
Mean of several analyses on macro scale ..	8·7	Nil	27·2	31·1	0·5	32·3
Standard deviation ..	0·05	—	0·37	0·35	0·20	0·35

NOTE—

Since this paper was written, some evidence has been privately communicated to us that, owing to the solubility of hydrogen in the ammoniacal cuprous chloride used to absorb carbon monoxide, there is a possible positive error in the macro-determination of hydrogen and a corresponding negative error in the value for carbon monoxide. The solubility of gases in aqueous potassium hydroxide has been noted, and it is probable that the determination of carbon dioxide on the macro scale is subject to a small positive error. From the evidence it seems that analyses on the micro scale, when dry reagents are used, are closer to the composition of the gas than uncorrected determinations on the macro scale, when wet reagents are used.

The authors are indebted to Mr. V. C. Broom for helpful discussion and valuable assistance in carrying out analyses on the macro scale. Acknowledgment is made to the Chief Scientist, Ministry of Supply, for permission to publish this paper. It is reproduced with the permission of the Controller of H.M. Stationery Office.

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A Semi-micro Gas Analysis Apparatus for the Determination of the Permanent Gases

BY G. J. MINKOFF AND N. V. V. PARTHASATHI

A semi-micro gas-analysis apparatus to analyse samples of from 0·5 to 3 ml of gas has been developed for the determination of carbon dioxide, hydrogen, oxygen, carbon monoxide, methane and nitrogen. No liquid or solid absorbents are used and no excess of gases has to be introduced to complete the determinations. The basic features of the method are the combination of oxygen with hydrogen and carbon monoxide in the presence of copper oxide at 285° C and the subsequent removal of excess of oxygen by copper, also at 285° C. The water and carbon dioxide formed are frozen out separately in solid carbon dioxide and liquid-air traps, and the pressure of the gas, in a constant volume, is measured at each stage. Should oxygen not be in excess, however, it is first made to combine with hydrogen and carbon monoxide in the presence of copper at 285° C, and the remaining hydrogen and carbon monoxide is then passed over the copper oxide. The pressures of the water and carbon dioxide formed indicate the original concentrations of the three gases. Methane is oxidised over the Arneil catalyst at 600° C, and the pressure of the remaining nitrogen is measured directly.

IN spite of the many different systems that have been described for the analysis of gases, there is still no method that is both accurate, rapid and versatile. A method is required to deal with as wide a range of gases and of gas volumes as possible. As a result, it is often simplest to design a new apparatus to meet specific needs. Thus, in combustion work, mixtures containing nitrogen, oxygen, hydrogen, methane, carbon monoxide and carbon dioxide, as well as hydrocarbons, often have to be analysed. The hydrocarbons, with the carbon dioxide, can be removed by passage through liquid air, and later dealt with by the usual infra-red method, the method of Bone and Newitt or other special methods. The non-condensable permanent gases present a fairly simple problem that can be treated in several ways. If techniques involving liquid reagents are neglected owing to the errors introduced by solubility, vapour pressures, and so on, then one of the most accurate methods described in the literature is that of Bamford and Baldwin,[1] whose apparatus handles volumes in excess of 10 ml. The low-pressure method of Strickland-Constable,[2] however, has many advantages, such as the small volume of sample and the short time required for absorption owing to the use of diffusion at low pressure to bring the gas molecules into contact with the reagents. Nevertheless, the presence of methane, and also of carbon monoxide, makes the application of the method more complicated. Nash's method[3] is useful as it makes use of solid reagents and it may be used for small gas samples.

The need is to develop an apparatus that would handle 0·5 to 3 ml of gas, that would not use liquid reagents, and that would avoid the addition of any hydrogen or oxygen to complete the analysis. The use of absorbants would also be avoided, as they usually cause inaccuracies except in low-pressure methods, such as Strickland-Constable's. As the system eventually devised combined several features of both the Bamford and Baldwin and the Nash techniques, a brief description of these two methods will now be given.

Bamford and Baldwin separated the constituents partly by cooling and partly by chemical methods not involving the use of confining liquids or absorbants. The resulting pressure changes were measured accurately by means of a balancing pressure of mercury together with a Foord gauge. Oxygen was determined by combustion with a known excess of carbon monoxide or hydrogen over a heated platinum wire, carbon monoxide and hydrogen by the reduction of copper oxide at 300° C, and methane was oxidised by copper oxide at 900° C. The water and carbon dioxide formed were frozen out separately in solid carbon dioxide and liquid-air traps at each stage. The analysis of small quantities of gas in the presence of 80 to 90 per cent. of nitrogen could be reproduced to approximately 0·01 per cent. of the total. The main disadvantages were: the use of copper oxide in silica at 900° C, which led to attack of the silica; the long time needed for an analysis; the use of the Foord gauge, which was liable to break; and the addition of gases to reduce the oxygen content, which increased the number of operations and of readings, thereby decreasing the accuracy.

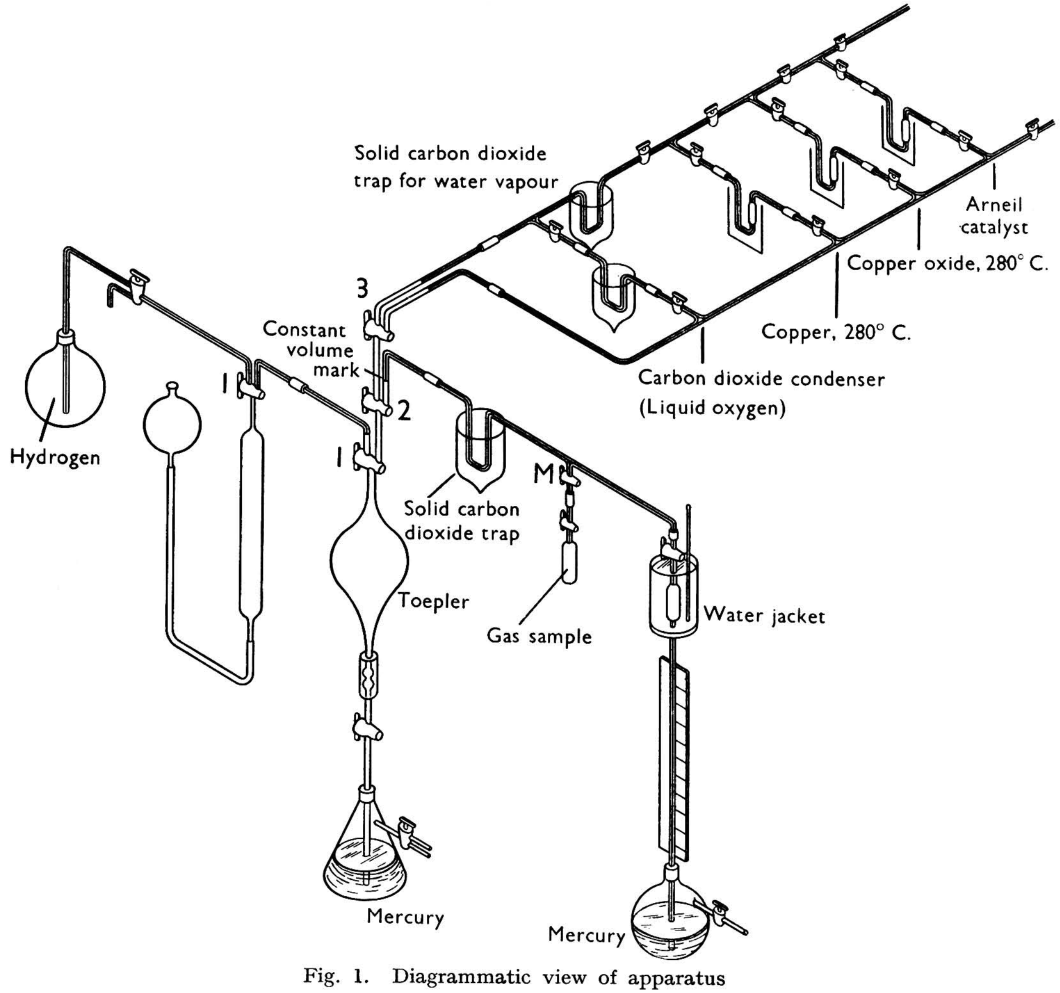

Fig. 1. Diagrammatic view of apparatus

The apparatus designed by Nash used volumes of gas down to 0·1 ml, a type of McLeod gauge being used for pressure measurements. This gauge was connected to a Toepler system, operated by water pressure, which was used for circulating the gases. The analytical train included anhydrone to remove water, liquid air for condensable vapours, ascarite (a soda-asbestos packing) to absorb carbon dioxide and a heated platinum wire. Hydrogen and carbon monoxide were separated from methane and excess of oxygen by fractional combustion over platinum at 475° C at low pressure. The methane was then burned on the platinum wire with an excess of oxygen at 850° C, and the remaining oxygen was ignited with an added excess of hydrogen. The advantages of this method include the pressure-measuring system and the small size of sample, but they are offset by the use of solid absorbants and by the need to add both oxygen and hydrogen. The interaction of platinum with oxygen above 700° C may also lead to errors, although low pressures were used to reduce this difficulty.

EXPERIMENTAL

The apparatus is shown diagrammatically in Fig. 1. The basic reactions are the oxidation of hydrogen and carbon monoxide by copper oxide at 285° C, the reduction of oxygen by copper at the same temperature, and the oxidation of methane at 600° C over the Arneil catalyst. The detailed mode of operation depends on whether oxygen or hydrogen + carbon monoxide is in excess, but in neither event is there any addition of gases to complete the analysis.

DESCRIPTION OF APPARATUS—

The three reagents and a trap containing solid carbon dioxide form four circuits, which are connected to a water-operated Toepler pump and manometer at one end and to a rotary vacuum pump at the other. The reactions are performed in small bulbs of about 2-ml capacity, connected to the apparatus through narrow capillaries. They are surrounded by electric furnaces maintained at the correct temperatures. The gas sample is introduced at M from a 3-ml sampling bulb. The gas is first drawn into the Toepler through a solid carbon dioxide trap to remove any moisture, and then it is passed into the manometer. The mercury in the right-hand limb of stopcock 2 is raised to a fixed mark so that the manometer measures the pressure of a constant reproducible volume of gas; the allowance made for the movement of the mercury in the capillary is described later. The atmospheric pressure and the temperature of the water jacket are always read. The gas is then withdrawn into the Toepler, three strokes being sufficient. The amount of gas sample was usually such as to give a pressure of about 150 mm in order to reduce errors from failure to obey Boyle's law. This was equivalent to just over 1 ml of gas at S.T.P.

Manometer—As the development of the apparatus was mainly of an exploratory character, the simplest manometer that would give the required accuracy was used. Evidently a much more satisfactory performance should result from the introduction of a McLeod device of the type used by Nash. The manometer used consisted of a bulb of 7-ml capacity, joined to a capillary tap above and to an 80-cm length of 0·8-mm capillary tubing. The lower part of the latter fitted through a rubber bung into a pool of mercury in a small flask, which could be evacuated when required, *i.e.*, during normal operation. As the manometer measured the pressure in the bulb, the volume of which was assumed to be constant, correction was made for the movement of the mercury in the capillary tube. The correction was calculated from Boyle's law, and it amounted to 0·8 per cent. of the reading at 100 mm, 2 per cent. at 300 mm and 3 per cent. at 400 mm.

PROCEDURE—

Carbon dioxide—This gas is first removed by passing the gas-mixture through a liquid-air trap three times; this operation takes about 10 minutes. The pressure is then measured again.

Carbon monoxide, hydrogen and oxygen—The procedure depends on the relative concentration of oxygen. If no approximate data on this is available, then a small portion of the sample may be tested as follows. The gas is circulated over copper and then over the copper oxide. If an excess of oxygen is present, the pressure readings after the first operation and after the second operation are the same, owing to the formation of water and carbon dioxide in the first operation and the removal of the excess of oxygen by the copper. The copper oxide consequently has no effect on the mixture. Alternatively, if excess of oxygen is not present, then any hydrogen and carbon monoxide that are not oxidised in the first operation will react with the copper oxide in the second operation, leading to a pressure change.

The analysis of a mixture containing an excess of oxygen is carried out by circulating the gas over completely oxidised copper oxide at 285° C. The hydrogen and carbon monoxide are oxidised with the consumption of an equivalent quantity of oxygen, so that the copper oxide behaves effectively as a catalyst. The carbon dioxide is frozen out in the liquid-air trap and the water in the solid carbon dioxide trap, the pressure being measured at each stage. The contractions indicate the concentrations of hydrogen and of carbon monoxide. The remaining gas, which contains oxygen, methane and nitrogen, is passed over bright reduced copper at 285° C to remove the oxygen.

If oxygen is not present in excess, it is removed by passing the mixture over freshly reduced, heated copper to convert the oxygen into water and carbon dioxide, which are frozen out in the usual way. The remaining hydrogen and carbon monoxide is now oxidised by passing it over heated copper oxide, and the water and carbon dioxide are again frozen out. The two amounts of both water and carbon dioxide then indicate the original concentrations of hydrogen, carbon monoxide and oxygen.

Methane and nitrogen—The gases left after the above operations are then passed over the Arneil catalyst[4] (99 per cent. of copper oxide + 1 per cent. of iron oxide containing 20 per cent. w/w of kaolin) at 600° C. This oxidises the methane to carbon dioxide and water, which are frozen out, and leaves nitrogen, the pressure of which is directly measured.

MAINTENANCE OF CATALYSTS—

To ensure the complete reduction of the copper catalyst, a small quantity of hydrogen is introduced from the reservoir every night. Next day it is removed with a rotary vacuum pump after the furnace has been switched on. The copper oxide and the Arneil catalyst are similarly treated with air.

The copper oxide is prepared by the method of Pieters.[5] Purified asbestos fibre is soaked in copper nitrate solution, dried and heated to 400° C. The asbestos is packed into the reaction tube, the oxide is reduced with hydrogen and then re-oxidised. Before the apparatus is used, a measured amount of oxygen is circulated through it to ensure that none is being retained.

RESULTS—

The analyses were usually reproducible to about ±0·5 per cent. of the sample; this was satisfactory for the present purpose.

CONCLUSION

Although the method has not yet been used extensively in this laboratory, it shows promise of meeting the requirements stated at the beginning of this paper. It avoids the use of solid absorbents, no gases have to be added, and a small sample can be analysed. The work that was done to develop the method therefore seems worth recording.

The authors' thanks are due to Professor Sir A. C. Egerton for suggesting the mode of attack on the problem and for his guidance and encouragement. The authors also thank Mr. Gooderham for the gift of the Arneil catalyst. One of us (N. V. V. P.) also wishes to thank the Government of India for a scholarship.

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The Spectrophotometric Determination of Small Amounts of Oxygen in Waters

By T. C. J. OVENSTON and J. H. E. WATSON

This paper describes the development of a method for the determination of dissolved oxygen in boiler feed waters applicable to concentrations in the range 0·001 to 0·1 ml of oxygen per litre, with a precision better than 0·001 ml at the lower concentrations. The method is based on that of Bairstow, Francis and Wyatt, but the precision is improved by avoiding the use of starch and by determining the liberated iodine by means of the ultra-violet absorption of the tri-iodide ion. The procedure has been simplified by the elimination of the step involving volumetric dilution before photometric measurement.

THE increasing use of high pressures in boiler plant has shown the need for a reliable method for the determination of concentrations of dissolved oxygen in feed waters at least as low as 0·002 ml per litre. An excellent review of the analytical methods available for the determination of oxygen has been given by Bairstow, Francis and Wyatt.[1] The most promising method now available appears to be that devised by these workers; this uses the same reaction as the well-known Winkler method, but the liberated iodine is determined absorptiometrically after the addition of starch. The effect of interfering substances is automatically compensated for by performing duplicate tests on each sample, in one of which the order of addition of the reagents is altered so that only the interfering substances react.

Bairstow *et al.* have paid close attention to the drawbacks associated with the use of the starch - iodine - iodide system for quantitative absorptiometric analysis, and they have included appropriate precautions in their procedure, such as the control of temperature, the recalibration with fresh starch stocks and the addition of a small amount of iodine to the system immediately before the addition of starch, to correct for the non-linear relation between the formation of the blue complex and the iodine concentration in the very low concentration ranges.[2] This method has been further studied by Pieters and Hanssen,[3] who showed that greater stability of the blue complex could be achieved by the addition of potassium sulphate. Nevertheless, they do not claim to determine oxygen contents below 0·0035 ml per litre.

METHOD

In another application, Ovenston and Rees[4] have drawn attention to the advantages to be gained over the starch method for determining small amounts of iodine, by making use of the strong absorption shown by the tri-iodide ion at 353 mμ. It was decided to apply this principle to the method of Bairstow *et al.* in an attempt to extend the range to cover lower concentrations.

The procedure finally adopted, given in detail below, is substantially the same as that recommended by these authors to the point at which the iodine is liberated, except that a higher concentration of potassium iodide is used to ensure satisfactory tri-iodide formation. Further manipulations have been simplified by arranging that a part of the solution is placed directly into the spectrophotometer cuvette without the necessity for any volumetric dilution; this enables maximum photometric sensitivity to be attained.

The samples of water of low oxygen content required for the development of this method were provided at first by passing a stream of pure nitrogen through a large aspirator containing distilled water. Subsequently, water from the outflow of a de-aerating condenser was used.

APPARATUS—

Sample tubes—These are similar to the Romijn pipettes described by Pieters and Hanssen, and they have a capacity of 50 ± 2 ml between the taps. Both stems carry zero graduation marks close to the taps and one stem is graduated at 0·2 ml beyond the zero mark while the other stem is graduated at 0·4 ml beyond the zero mark. The volume between the taps and the zero marks is unimportant. A pair of these sample tubes is required for each determination.

The internal surfaces of the tubes must be free from adsorbed impurities capable of reacting with potassium iodide. It has been found satisfactory to cleanse the tubes with warm water containing Teepol, followed by copious rinsing with pure water then with warm dilute sulphuric acid, and further rinsing with water. On no account should chromic acid mixture be used.

REAGENTS—

All reagents should be of recognised analytical grade.

Alkaline potassium iodide solution—Dissolve 300 g of sodium hydroxide and 430 g of potassium iodide in water and make up to 1 litre.

Manganous sulphate solution—Dissolve 450 g of manganous sulphate tetrahydrate in water and make up to 1 litre.

Sulphuric acid, approximately 18 N.

Standard iodine solution, for the preparation of the calibration graph—Prepare a preliminary solution by dissolving 1·2 g of iodine and 10 g of potassium iodide in 1 litre of water, and standardise the solution with 0·01 *N* thiosulphate. Dilute accurately a suitable aliquot 500 times with distilled water to give the standard solution (containing about 2·4 μg of iodine per ml).

Potassium iodide solution, for the preparation of the calibration graph—Prepare a 21·5 per cent. w/v aqueous solution of potassium iodide by dissolving the solid in distilled water.

Before use, the first three reagents must be de-oxygenated. This is done by passing a stream of oxygen-free nitrogen through each reagent for about half an hour, preferably when the reagent is in its storage bottle. The latter should be fitted permanently with an alkaline pyrogallol solution trap at the inlet, through which a slight pressure of nitrogen can be applied subsequently in order to facilitate delivery of the reagent by way of an outlet tube fitted with a tap. The end of the delivery jet should be narrow enough to allow it to reach the base of the stem of the sample pipette.

PROCEDURE—

Feed the water to be tested through a Y-tube connected, by means of rubber tubing fitted with screw clips, to the lower stems of two sample pipettes. Allow the water to flow up and out at the top stems and lead it to waste through rubber tubing. Take care that no air bubbles are trapped in the pipettes. Pass at least 300 ml of the sample through each pipette, then stop the flow, close the top taps of the pipettes and tighten the screw clips. Remove the rubber tubing from the top stems and also the Y-tube from the tubing attached to the lower stems.

The lower taps on the pipettes should not be closed until the actual determination can be carried out, which should be delayed as little as possible after taking the samples. As the sample is usually warmer than room temperature, a gradual contraction takes place inside the pipette, but the elasticity of the piece of rubber tubing attached to one end of each pipette offsets the risk of air being drawn into them.

Clamp the pipettes vertically, side by side, with the stems bearing the 0·4-ml graduation uppermost. Allow them to stand for 5 minutes, then close the second pair of taps and remove the tubing. Remove the bulk of the water left in the stems. (A narrow tube connected to a filter-pump is useful for this purpose.) Remove the last traces of water from the stems by means of filter-paper and fill them to the 0·4-ml graduation with alkaline potassium iodide reagent, taking care to prevent needless contact with air. Introduce 0·4 ml of the reagent into each pipette by opening first the upper taps and then controlling the flow by means of the lower taps until the level of the reagent has fallen to the zero graduation; then close all taps again, the lower taps first. Mix the contents of the pipettes by a rocking motion, replace the pipettes in the clamps in the same position and wash out the stems with distilled water. Invert the pipettes and dry the stems with filter-paper, the 0·2-ml graduation now being uppermost.

Fill the stem of one of the two pipettes (the oxygen-determination pipette) to the 0·2-ml graduation with manganese sulphate reagent, and introduce 0·2 ml of the reagent into the pipette as already described. Mix the contents and allow the pipette to stand for about 3 minutes, rocking it once or twice during this period, to ensure complete reaction between the precipitated manganous hydroxide and the dissolved oxygen. Wash the pipette, dry the same stem again and then introduce 0·2 ml of 18 *N* sulphuric acid. Rock the pipette occasionally during 3 minutes to ensure complete dissolution of the precipitate.

At the same time introduce 0·2 ml of 18 *N* sulphuric acid followed by 0·2 ml of manganous sulphate reagent into the other pipette (the blank-determination pipette). No precipitate is formed in this pipette, and the time intervals between the introductions of reagents are not important.

Wash out the uppermost stem (with 0·2-ml graduation) of each pipette and dry it. Open the upper taps and by means of the lower taps allow sufficient of the solutions to pass through the lower stems to ensure that the liquid trapped in the bores of the lower taps is washed away. (The entry into the pipettes at this stage of the small amount of acid left in the bores of the upper taps does not matter.)

Fill 4-cm cuvettes with the remaining solutions and measure their optical densities at 353 mμ by means of a spectrophotometer. (Measurements must be made within 20 minutes of the introduction of the acid into the pipettes.) Deduct the optical density of the blank from that of the oxygen sample and determine the oxygen content of the water from the calibration graph.

PREPARATION OF THE CALIBRATION GRAPH—

Measure into separate 50-ml calibrated flasks 0·5, 1, 2, 3, 4, 5, 10, 20, 30, 40 and 50-ml volumes of standard iodine solution and make each aliquot up to 50 ml with distilled water. To each flask add 0·8 ml of 21·5 per cent. w/v potassium iodide and mix the contents. The omission of the sodium hydroxide, sulphuric acid and manganous sulphate does not affect the slope of the calibration graph, but does improve the stability of the standards.

Prepare at the same time a blank consisting of 50 ml of water (free from standard iodine solution) to which 21·5 per cent. w/v of potassium iodide has been added, as described for the standards.

Measure the optical density at 353 mμ of each standard and of a blank in 4-cm cuvettes. Deduct the optical density of the blank from each of the standard optical densities, and plot the differences against concentration of dissolved oxygen in ml per litre, knowing the actual quantity of iodine added to each standard and noting that 1 mg of iodine (in 50 ml) is equivalent to 0·882 ml of oxygen per litre.

In practice it is convenient to construct a separate calibration graph for the lower part of the range, covering optical densities up to 0·1 as found from the first six standards.

OXYGEN IN REAGENTS—

Owing to the fact that any oxygen in the reagents is active in the oxygen-determination sample and not in the blank-determination sample, because of the altered order of addition of reagents to the latter, it has been the custom of earlier workers[1,3] to correct the final result by deducting the amount of oxygen present in the small volumes of added reagents. This correction was usually about 0·005 ml of oxygen per litre.

For the present purpose it was considered that a correction of this magnitude, liable to slight variation, would materially reduce the accuracy of the method at the lower end of the range. By de-oxygenating the reagents as described, the oxygen content can be reduced to a negligible amount, which makes a correction unnecessary.

CONCENTRATION OF POTASSIUM IODIDE—

The alkaline iodide reagent used by Bairstow *et al.* contained only sufficient iodide to bring the iodide molarity of the final solution to between 0·003 and 0·004. At this concentration significant dissociation of tri-iodide occurs and the proposed method of measurement would not be feasible.

By increasing the iodide concentration of the reagent to 430 g per litre and the volume taken to 0·4 ml, the final molarity was raised to 0·02. Although this is still lower than the value of 0·1, which is regarded as ideally desirable for this system,[4] only an insignificant loss in sensitivity occurs, and an error of 5 per cent. in the reagent addition results in one of but 0·5 per cent. in the determination.

LINEARITY OF CALIBRATION—

In the analytical range for which this method is designed, the calibration graph is a straight line passing through the origin. No deviation from Beer's law occurs at the lower concentrations in contrast to that observed when starch is used.

With a Unicam model SP500 spectrophotometer set at 353 mμ, it was found that 0·1 ml of oxygen per litre in the sample was equivalent to an optical density of 0·82 for a 4-cm optical depth.

STABILITY AND EFFECT OF TEMPERATURE—

The stability with time of the iodine - iodide - tri-iodide system depends on pH, being greatest for nearly neutral solutions. It is inevitable after the dissolution of the manganous hydroxide that the residual solution should be slightly acid and the residual acid normality is about 0·01. The conditions, therefore, correspond to those for experiment B described in the earlier paper by Ovenston and Rees,[4] from which it may be judged that sufficiently reliable results can be expected at this acidity provided that the taking of measurements is not long delayed.

In practice it has been found that the results are satisfactory when the spectrophotometric measurements are made within 20 minutes of the acidification of the solution. Any scheme for the batching of samples for routine analytical purposes should therefore take this into account.

Slight variations of temperature within a range of 10° C do not affect the extinction coefficient of the solution significantly, but it is preferable for the working temperature to be kept as low as is convenient because the stability of the tri-iodide decreases with rise in temperature. It is necessary for the solutions after acidification to be shielded from direct sunlight for a similar reason.

EFFECT OF IMPURITIES—

With the twin pipette technique, in which the oxygen is allowed to contribute to the total iodine release in only one of the pipettes, the effect of other oxidising impurities in the water is automatically compensated for, provided that these impurities are in solution. Care must still be taken to avoid small pieces of oxide scale from finding their way into one of the pipettes.

The method similarly compensates for very small amounts of reducing impurities in solution, provided these are not sufficient to reduce the optical density of the blank to zero. A zero blank optical density would indicate the presence of a probable excess of reducing impurity, and the determination would accordingly be rendered useless. If excessive amounts of reducing impurities are present, these can be compensated for by dissolving a sufficient quantity of iodine in the alkaline potassium iodide reagent to ensure a positive blank optical density.

REPRODUCIBILITY OF RESULTS

For the purpose of checking the reproducibility of the method for low oxygen contents a series of determinations was carried out in duplicate, that is, one blank and two oxygen determinations per set. The results, shown in Table I and found by an analyst already familiar with the method, suggest that the method can provide useful analytical figures to 0·001 ml or less of oxygen per litre.

COMMENTS ON A POSSIBLE EXTRACTION MODIFICATION

The sensitivity of the method would be improved if the liberated iodine could be concentrated by extraction into a comparatively small volume of chloroform or carbon tetrachloride. For this purpose it would be necessary to reduce the iodide content of the alkaline potassium iodide reagent to the absolute minimum in order to encourage dissociation of the tri-iodide complex.

There would be no point in extracting into such a solvent in order to measure the optical density of the molecular iodine in that solvent, because the extinction coefficient of iodine in such solvents at 510 mμ is only about one-thirtieth of that of iodine, as the tri-iodide complex, at 353 mμ. However, it has been found[5] that, by adding an equal volume of alcoholic potassium iodide to a solution of iodine in chloroform or carbon tetrachloride, the iodine is practically completely converted to tri-iodide, and in this composite medium there is an extinction maximum at 360 mμ having about the same molar value as is found at 353 mμ in aqueous solution. With this reaction it would be necessary, therefore, to reduce the total volume of the solvent extract only to one-half in order to equal the sensitivity attainable without extraction and any further reduction should result in a gain.

An extraction procedure based on these principles was tried, but was abandoned because of the difficulty found in attaining reproducible extraction.

TABLE I

RESULTS FOR THE DETERMINATION OF OXYGEN IN WATERS OF LOW OXYGEN CONTENT

E_{blank}	$E_{samples}$	$E_{diff.}$	Oxygen per litre, ml	Duplicate differences
0·013	0·143	0·130	0·0151	0·0004
	0·146	0·133	0·0155	
0·015	0·071	0·056	0·0065	0·0007
	0·077	0·062	0·0072	
0·014	0·056	0·042	0·0049	0·0006
	0·051	0·037	0·0043	
0·013	0·198	0·185	0·0215	0·0005
	0·194	0·181	0·0210	
0·004	0·056	0·052	0·0060	0·0004
	0·052	0·048	0·0056	
0·007	0·084	0·077	0·0090	0·0005
	0·089	0·082	0·0095	
0·004	0·041	0·037	0·0043	0·0002
	0·043	0·039	0·0045	
0·004	0·040	0·036	0·0042	0·0004
	0·037	0·033	0·0038	
0·003	0·046	0·043	0·0050	0·0002
	0·048	0·045	0·0052	

ADAPTATION FOR USE WITH THE SPEKKER ABSORPTIOMETER

For the best results a spectrophotometer having a high performance in the near ultraviolet region is required. However, with a slight sacrifice of precision, a Spekker absorptiometer (or similar filter instrument) with a mercury-arc source may be used with Wood's glass filters. In order to make use of all the available radiant energy, the Spekker absorptiometer should be calibrated by setting the drum at zero with the standard in the light beam, and the drum difference is measured after moving in the blank. Similarly, when making the determination, the drum should be set to zero with the sample in the beam.

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ADMIRALTY MATERIALS LABORATORY
HOLTON HEATH
POOLE, DORSET

November 9th, 1953

Notes

IDENTIFICATION OF PHENOL

An easily produced, yet little known, compound of phenol and hexamine (hexamethylenetetramine) can be used for the identification of phenol, either alone or in presence of the cresols.

The compound, which seems to have been first described by Moschatos and Tollens[1] in 1891, is considered to be composed of 3 molecules of phenol combined with 1 molecule of hexamine. This composition was confirmed by Harvey and Baekeland,[2] although Smith and Welch[3] considered it to be a 1 + 1 addition compound. Some account of the substance is given by Ellis.[4] The composition does not seem, however, to be of much importance where the test is concerned, as the formation of the needle-like crystals from dilute solution is so distinctive and can be readily observed. As the crystals decompose on melting at between 100° and 125° C, according to the solvent from which they are recrystallised, there is no sharp melting point that can be used for purposes of identification; but, in the author's opinion, the distinctive appearance and conditions of formation of the crystals render such extra identification unnecessary.

The compound is readily produced by adding a strong solution of hexamine to phenol saturated with water. If a solution of phenol in water is used, the formation of needle-like crystals can be observed. The reaction is best carried out on a watch-glass by adding 3 or 4 drops of saturated hexamine solution to 1 ml of phenol solution. By this method, phenol alone in aqueous solution can be identified at as low a concentration as 4 per cent. If crystals do not form immediately, the mixture is allowed to stand on the watch-glass for a while; crystals will then begin to form from the edge of the liquid as evaporation proceeds, 5 to 10 minutes being a sufficient time for the needle-like crystals to be observed, especially if a lens is used. Crystallisation can be hastened by scratching with a glass rod. As the crystals are fairly soluble in water, addition of an excess of hexamine solution must be avoided, as this increases the volume of water unduly and so prevents crystallisation.

The cresols also produce similar compounds, but by no means so readily as phenol itself, it being necessary to use the cresol layer of the cresol - water mixture, and even then the *o*-cresol compound is difficult to obtain. A saturated solution of the cresols does not yield crystals under the conditions described.

If, therefore, a mixture is being examined, and by odour and general reactions it is obviously phenolic in character, the presence of phenol can be demonstrated by the following procedure. The mixture is shaken with water and the phenolic layer is allowed to settle. Then to 1 ml of the aqueous layer are added 3 or 4 drops of saturated hexamine solution, the reaction being carried out on a watch-glass as described previously. The formation of the needle-like crystals can be taken as evidence of the presence of phenol. The author has found that the presence of up to a total of about 40 per cent. of all or any of the cresols before the sample is shaken with water does not interfere with the test.

As nearly all the usual tests described for phenol are responded to similarly by the cresols, the test here described should be useful, as it is simple to perform and is specific for phenol.

IDENTIFICATION OF FORMALDEHYDE

By the converse of the above reaction, solutions of formaldehyde as dilute as 4 per cent. can be identified, the required hexamine being formed in the solution.

About 0·05 g of phenol crystals are placed on a watch-glass, and just sufficient of a 1 + 1 mixture of ammonium hydroxide, sp.gr. 0·880, and water is added dropwise to dissolve the crystals. Up to about 10 drops of the suspected formaldehyde solution are then added. If the liquid becomes turbid owing to the formaldehyde reacting with the ammonium hydroxide, a drop or two more of ammonium hydroxide is added just to clear it. The solution is then allowed to stand for a few minutes, when the typical needle-like crystals are observed forming at the edges if formaldehyde is present.

As formaldehyde is the only aldehyde that yields the necessary hexamine, the test is specific.

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E. Hough

First submitted, *June 30th*, 1953
Amended, *January 5th*, 1954

Apparatus

AN APPARATUS FOR PAPER PARTITION CHROMATOGRAPHY

(*Demonstrated at the Meeting of the Microchemistry Group on Friday, January 29th,* 1954)

DISADVANTAGES of the conventional methods of paper partition chromatography are inherent in the size of vessel required. It is usual to suspend the paper in a vertical plane and therefore the dimensions of the vessel used must exceed those of the paper. If the best results are to be attained, the atmosphere inside the chamber should be saturated with respect to the solvents used. The time required for the attainment of this equilibrium is a function of the volume of air to be saturated, and with a large volume this may be considerable. Satisfactory chromatograms are also dependent on the maintenance of a constant and uniform temperature within the apparatus. This requirement may be difficult to fulfil with large vessels, particularly when it is desired to make the chromatograms at temperatures other than that of the laboratory. The use of a small-scale technique, such as the Rutter method,[1] obviates these difficulties, but the great reduction in the size of the paper and the radial development, with the consequent difficulty of measuring R_F values, limit its usefulness. Meredith and Sammons[2] have described an all-glass apparatus for horizontal paper chromatography in which some reduction in size is effected by folding the paper, which is supported by a glass frame. In the "Chromatocoil" designed by Schwarz[3] space is saved by coiling the paper in a metal holder, which is enclosed in a glass jar. The strip may be of considerable length, but is necessarily very narrow, so that control spots cannot be run on the same paper.

This Note describes a simple, robust and compact apparatus that overcomes all the above disadvantages. By winding the paper in a coil, the volume has been greatly reduced and the over-all size of the apparatus is such that it can easily be maintained at any desired working temperature. The apparatus, which is shown in Fig. 1, consists of a coil, a chamber and lid, and solvent troughs. Each part will be described separately.

COIL—

This consists of a piece of stainless-steel gauze (mesh 10 B.S.S.), 6·5 inches wide and 24 inches long, wound into a loose spiral of outside diameter 4 inches and soldered at one end to a circular metal plate of diameter 4 inches. The turns of the spiral are about ½ inch apart. A stainless-steel rod of diameter ¼ inch and threaded at both ends passes longitudinally through the centre of the coil and through the plate to which it is attached, projecting 1¼ inches at each end.

CHAMBER—

A metal vessel of inverted U-section having a flat base and one open and one closed end. Its over-all dimensions are a length of 6·9 inches, a width of 4·9 inches and a height of 5·8 inches. A hole to take the centre-rod of the coil is drilled in the closed end of the chamber, 3·5 inches from the base, so that when in position the coil is in the upper part of the chamber. Passing horizontally through the closed end is an inlet tube (internal diameter ⅛ inch) that is bent downwards so that it will deliver into the middle solvent trough. The outer end of this tube is closed by a threaded plug.

LID—

The lid that closes the open end of the chamber has a peripheral flange. Attached to it is a smaller, similarly flanged plate. The groove formed by the two flanges contains an asbestos gasket to make a seal between the lid and the chamber. A hole to take the centre rod of the coil is drilled in the lid in a position corresponding to that in the closed end of the chamber. The coil and lid are held in position by washers and wing-nuts, screwed up on the projecting threaded ends of the centre rod of the coil.

SOLVENT TROUGHS—

Three rectangular metal trays that fit into the bottom of the chamber. Their dimensions are 1·2 inches × 6·6 inches × 0·9 inch.

MATERIALS—

The apparatus described and illustrated is made entirely of stainless steel. Earlier models made of heavily-tinned brass (except the coil, which has always been of stainless steel) have also given satisfactory service when used with many, but not all, solvents.

METHOD OF USE

The apparatus is capable of taking a strip of paper 15 cm wide and up to 60 cm long. Apply the spots of solution in the normal way and wind the paper on the coil so that the end with the spots is on the outside. About 10 cm of the paper should project beyond the end of the coil. Place the coil in the chamber, securing it in position by means of the washer and nut at the back. Put the solvent troughs in position on the base of the chamber and add about 10 ml of the solvents to each of the two outer troughs. The free end of the paper should be arranged in the middle trough, which is left empty at this stage. A small strip of stainless-steel gauze placed on the end of the paper will ensure that it does not subsequently move out of place. Put on the lid and fasten it in position by means of the washer and nut. Set the apparatus aside in the place in which it is to be used and allow a few hours to elapse so that a state of equilibrium can be reached within it between the solvents, the internal atmosphere and the paper.

Add an appropriate volume, about 25 ml, of the developing solvent through the inlet tube at the back. This can conveniently be done by means of a hypodermic syringe with a wide-bore needle. In this way the solvent may be added without disturbing the equilibrium that has already been reached in the chamber. The solvent should be at the temperature of the apparatus before it is added (see below).

TABLE I

THE VARIATION OF R_F WITH TEMPERATURE FOR SOME SUGARS

Solvent: *n*-butanol saturated with water at the working temperature
Paper: Whatman No. 1

Sugar	Values of $R_F \times 100$ at 0° C	20° C	37° C	50° C
Melezitose	0·3	0·5	1·5	4·4
Maltose	0·8	1·5	3·5	6·7
Sucrose	1·5	2·8	5·8	9·6
Galactose	3·5	5·3	10·9	13·9
Glucose	4·7	7·5	12·3	15·8
Mannose	7·6	9·3	15·8	19·6
Xylose	10·4	14·0	20·2	24·8
Rhamnose	19·1	24·4	31·9	36·9

Development is allowed to continue for an appropriate duration of time. As the progress of the solvent front cannot be seen, it is necessary to be guided by previous experience with the particular solvents, paper and conditions used. Alternatively, the rate of movement of the solvent front may be estimated by the method of Müller and Clegg.[4] Development should be stopped before the solvent front reaches the end of the paper, as the apparatus cannot be used for elution chromatography. When long development is necessary, a second strip of paper may be attached and wound round the centre rod of the coil.

The apparatus was designed for one-dimensional chromatography, but it can be used for the two-dimensional method devised by Boggs.[5]

DISCUSSION

The apparatus described was developed to facilitate chromatography at different temperatures, and it is for this purpose that it is most useful. Its small dimensions allow it to be used in a normal-sized refrigerator, incubator, low-temperature oven or other suitable air-bath. Its small internal volume results in the rapid attainment of equilibrium between solvents, internal atmosphere and paper. As it is constructed entirely of metal, it quickly reaches thermal equilibrium with the ambient atmosphere.

At elevated temperatures the solvent front moves more quickly with a consequent reduction in the time required for the development of the chromatogram. Hough, Jones and Wadman[6] considered that the chromatography of sugars and methylated sugars was markedly improved at 37° C. They reported faster movement, improved definition of the spots and higher R_F values. We have made chromatograms of sugars, with a series of solvents, throughout the temperature range 0° to 50° C and have confirmed the dependence of R_F values on temperature. In all the examples examined, the R_F values were increased by a rise in temperature. Table I shows some of the results. The higher R_F values, together with the faster movement, render the use of elevated temperatures

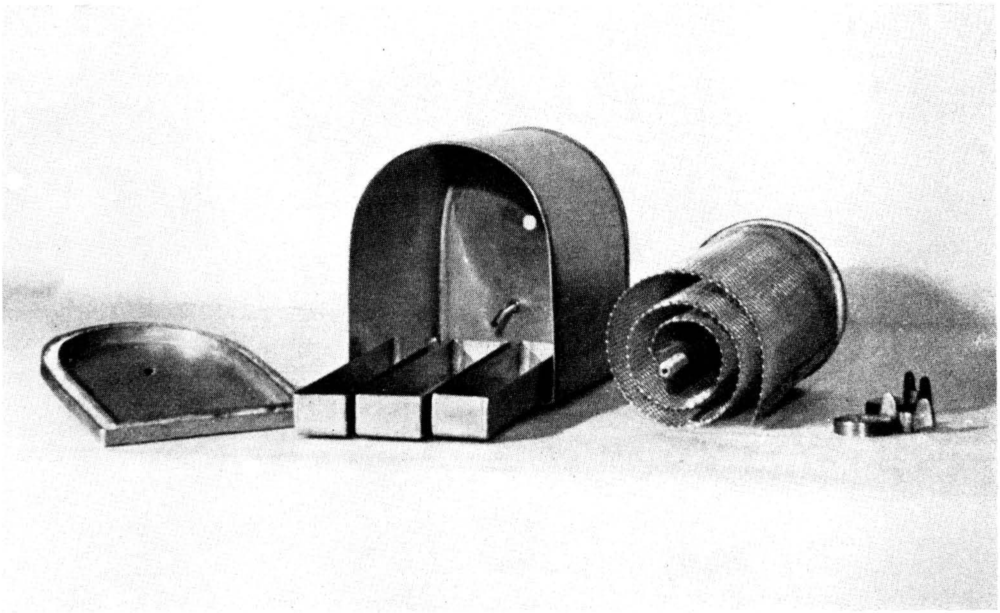

Fig. 1. Details of apparatus

doubly advantageous. For example, some di- and tri-saccharides that do not move measurable distances in 24 hours at 20° C give readable R_F values after development with the same solvent for 16 hours at 50° C. We are continuing to investigate the effects of temperature on the chromatography of sugars and intend to publish a study of this subject and its implications.

It is important that the developing solvent should be at the working temperature before it is introduced into the chamber. When an immiscible solvent is used, the phases should be allowed to equilibrate at the working temperature before separation, as the compositions of the phases may be markedly different at different temperatures. Doubtless this fact is partly responsible for the effect of temperature on R_F values.

This apparatus has been in regular use for over a year and has been used at temperatures from 0° to 50° C with satisfactory results.

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December 14th, 1953

Home Office

STATUTORY INSTRUMENTS*

1953—No. 1300. The Poisons List Order, 1953. Price 4d.

This Order, which came into operation on September 1st, 1953, *adds certain substances to the Poisons List and, in the Third Schedule, sets out the complete list. A drafting amendment has been made in the item relating to amidopyrine, and the substances dextrorphan, levorphan and racemorphan, hitherto included in the list under the name methorphinan, which is no longer in use, are shown separately in the new list.*

The Order refers to the Pharmacy and Poisons Act, 1933, *and to the Third Schedule to the Poisons List Order,* 1952 (*S.I.*, 1952, *No.* 2085).

1954—No. 266. The Poisons List Order, 1954. Price 2d.

This Order, which came into operation on April 1st, 1954, *adds to Part I of the Poisons List* (*see above*) *the item "Tri-2(-chloroethyl)amine; its salts."*

Ministry of Food

STATUTORY INSTRUMENTS*

1954—No. 613. The Food Standards (Margarine) Order, 1954. Price 4d.

This Order, which came into operation on May 16th, 1954, *should be read with the Food Standards (General Provisions) Order,* 1944 (*S.R. & O.*, 1944, *No.* 42; *Analyst*, 1944, **69**, 49), *as amended* (*S.R. & O.*, 1944, *No.* 654; *Analyst*, 1944, **69**, 247). *It prescribes a standard for margarine as respects vitamin A and vitamin D to be contained therein, and a method for the determination of vitamin A based upon double-column chromatographic extraction of the unsaponifiable matter followed by a spectrophotometric procedure.*

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* Obtainable from H.M. Stationery Office. Italics indicate changed wording.

British Standards Institution

NEW SPECIFICATIONS *

B.S. 1673 : Part 2 : 1954. Methods of Testing Raw Rubber and Unvulcanized Compounded Rubber. Part 2: Methods of Chemical Analysis. Price 7s. 6d.

B.S. 2087 : 1954. Chemical Requirements for Textiles Treated by Certain Preservative Processes. Price 4s.

B.S. 2463 : 1954. Transfusion Equipment for Medical Use. Price 3s.

* Obtainable from the British Standards Institution, Sales Department, 2, Park Street, London, W.1

DRAFT SPECIFICATION

A FEW copies of the following draft specification, issued for comment only, are available to members of the Society, and can be obtained from the Secretary, Society for Analytical Chemistry, 7–8, Idol Lane, London, E.C.3.

Draft Specification prepared by Technical Committee LBC/14—Laboratory Ovens.

CT(LBC)3072—Draft B.S. for Performance Requirements for Laboratory Ovens.

Book Review

MISES AU POINT DE CHIMIE ANALYTIQUE PURE ET APPLIQUÉE ET D'ANALYSE BROMATOLOGIQUE. Publiées sous la direction de J.-A. GAUTIER. Pp. iv + 172. Paris: Masson et Cie. 1953. Price 1400 fr.

This volume is the first of an annual series of reviews on analytical chemistry and the analysis of foodstuffs. The preface by Professor Fabre indicates that the purpose of these reviews is to enable working analysts to keep abreast of developments in analytical chemistry.

Two useful reviews on subjects of general interest are included, *viz.*, acid - base titrations in non-aqueous solvents and the use of Complexones in analytical chemistry; the latter has an extensive bibliography. The rest of this volume is devoted to food analysis—the normal contents of the commoner metallic elements in foodstuffs, the determination of acetaldehyde in wines and spirits, analytical control in the baking industries, the natural variations in the composition of milk, and the examination of edible oils and fats.

The paper on the determination of acetaldehyde in wines and spirits, as one might expect, is the one likely to attract most attention in this country and, indeed, this paper merits study.

Some of the subjects dealt with are dismissed in too cursory a fashion to be of any but a general interest and lack an adequate biblography, which detracts even further from their usefulness. This particularly applies to the section on analytical control in the baking industry and that on the examination of edible oils and fats, which is a rather indiscriminate survey of the subject. It seems odd for instance, to find no mention of the Kreis test even in a short account of methods of evaluating rancidity.

The printing is good and the diagrams and tables clearly set out; the production is typically French.

P. MORRIES

Publications Received

YEAST TECHNOLOGY. By J. WHITE, B.Sc., F.R.I.C. Pp. xvi + 432. London: Chapman & Hall Ltd. 1954. Price 55s.

SILAGE FERMENTATION. By A. J. G. BARNETT, B.Sc., Ph.D., F.R.S.E. Pp. x + 208. London: Butterworths Scientific Publications; New York: Academic Press Inc. 1954. Price 27s. 6d.

QUANTITATIVE ORGANIC ANALYSIS VIA FUNCTIONAL GROUPS. By S. SIGGIA, Ph.D. Second Edition. Pp. x + 227. London: Chapman & Hall Ltd.; New York: John Wiley & Sons Inc. 1954. Price 40s.; $5.00.

METHODS OF BIOCHEMICAL ANALYSIS. Volume I. Edited by D. GLICK. Pp. x + 521. New York and London: Interscience Publishers Inc. 1954. Price $9.50; 75s.

A TEXT-BOOK OF MACRO AND AND SEMIMICRO QUALITATIVE INORGANIC ANALYSIS. By A. I. VOGEL, D.Sc., D.I.C., F.R.I.C. Fourth Edition. Pp. xviii + 663. London and New York: Longmans, Green & Co. Ltd. 1954. Price 22s.

RECOMMENDATIONS FOR THE DISPOSAL OF CARBON-14 WASTES. National Bureau of Standards Handbook 53. Pp. vi + 14. Washington: U.S. Government Printing Office. 1953. Price 15 cents.

CHIEF ANALYST. Applications are invited from men over 30 to take charge of the modern and well-equipped laboratory engaged mainly on inorganic analysis at our Battersea headquarters. Ability to control staff of 15 analysts, and to co-operate with other technical staff, are as important as professional qualifications. The company has good welfare facilities, including pension scheme and five-day week, and the post offers a permanent and attractive career to the right man. The salary to be agreed will be commensurate with the position. Write, giving details of age, experience and qualifications to the Staff Manager, The Morgan Crucible Co. Ltd., Battersea Church Road, London, S.W.11.

COUNTY COUNCIL OF DURHAM

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AND AGRICULTURAL ANALYST

APPLICATIONS are invited for the above posts from persons who are qualified in accordance with the Public Analysts' Regulations, 1939, and the Fertilisers and Feeding Stuffs Act, 1926.

The salary scale will be £1,500 rising by annual increments of £50 to a maximum of £1,750 per annum, and the commencing salary will be determined according to qualifications and experience. The appointment will be subject to the provisions of the Local Government Superannuation Acts, the approval of the Minister of Food and the Minister of Agriculture and Fisheries and the passing of a medical examination and will be terminable by three months' notice in writing on either side.

Applications, stating age, qualifications and full details of experience and appointments held, together with the names and addresses of three referees, must be received by the undersigned not later than Wednesday, 30th June, 1954. Applicants should also state the probable date they could take up duties if appointed.

The person appointed will be required to devote the whole of his time to the duties of the office.

J. K. HOPE,
Clerk of the County Council.

SHIRE HALL, DURHAM.
7th May, 1954.

ANALYTICAL CHEMISTS. The partners in an old established London firm of Analytical Chemists desire to make provision for eventual retirement by sale, amalgamation, or the admission of a younger partner. Terms to be discussed. Those interested should write to Lamartine Yates & Lacey, Solicitors, 61, Carey Street, Lincoln's Inn, London, W.C.2.

CHEMIST required for development and research in the manufacture of aromatic chemicals and to supervise production in the London Factory of an International Company. A good knowledge of essential oils an advantage. Permanent progressive position. Please reply to Box No. 3860, THE ANALYST, 47, Gresham Street, London, E.C.2.

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METALLURGICAL CHEMIST required to supervise and participate in the work of the analytical section of the chemical laboratory. The work is not routine and is concerned mainly with ferrous and non-ferrous materials. The applicant should have a degree or similar qualifications as well as several years' experience in the field of ferrous analysis. Applications giving full details should be made to The Director of Research, G.K.N. Group Research Laboratory, Birmingham New Road, Lanesfield, Wolverhampton.

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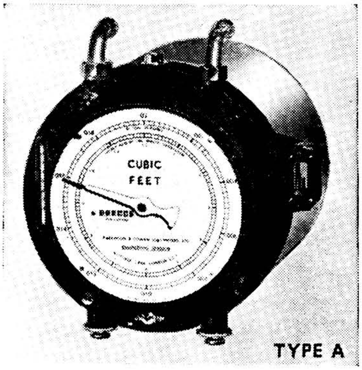
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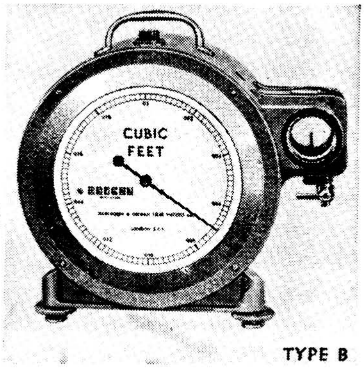
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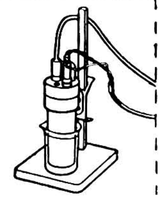

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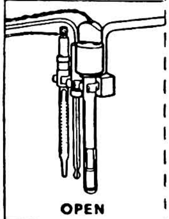

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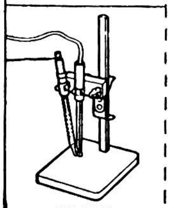

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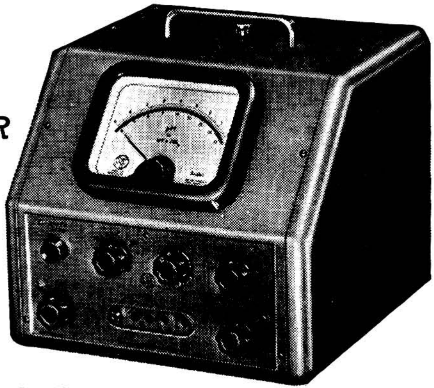

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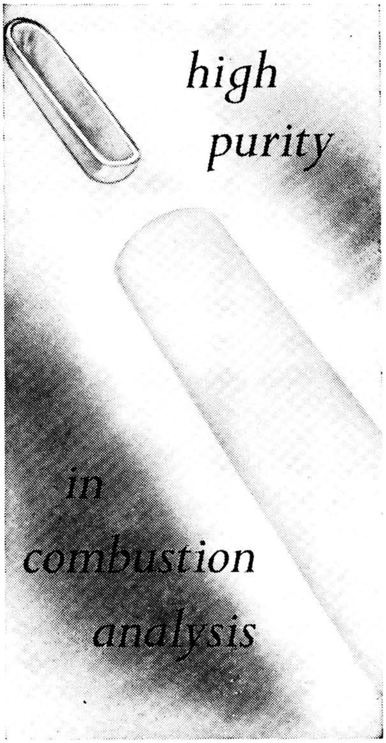
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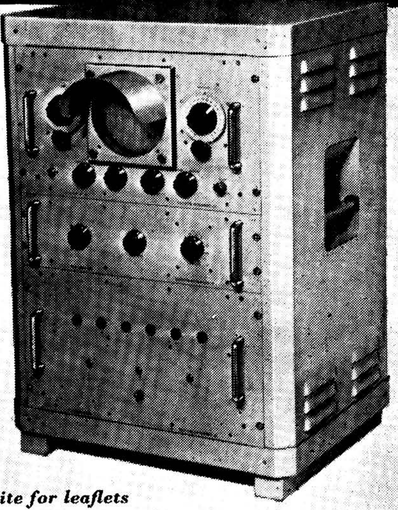

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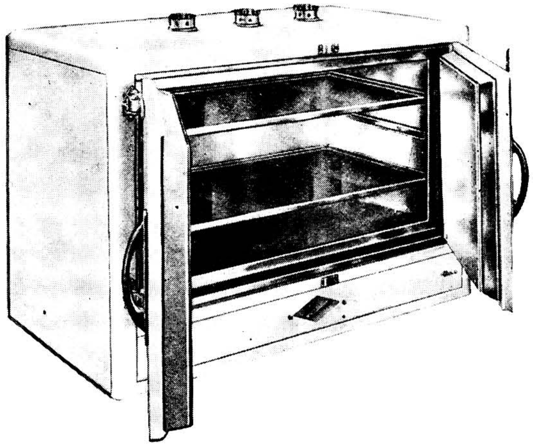

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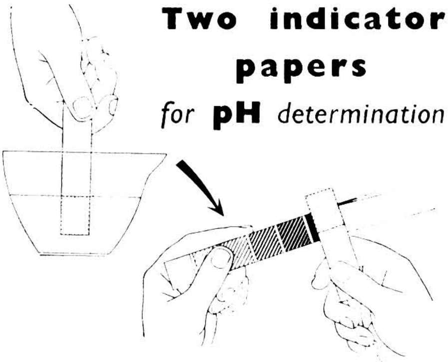

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