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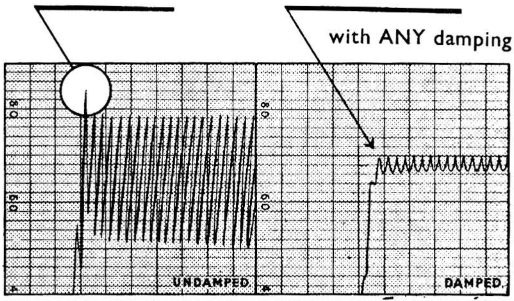

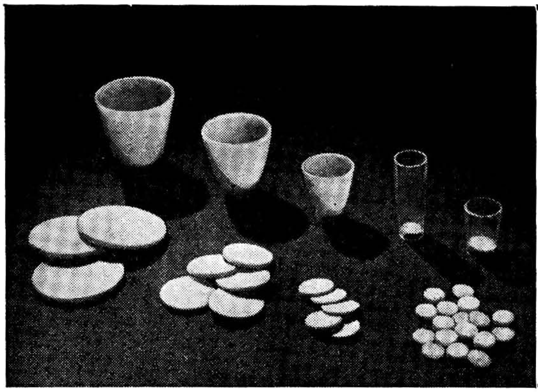

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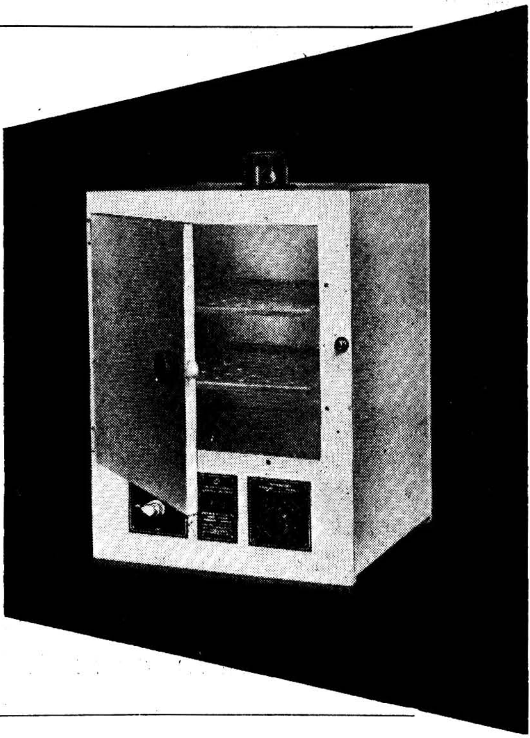


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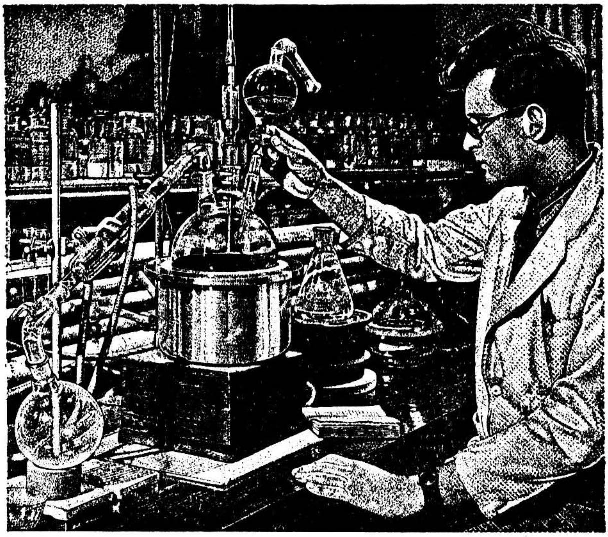

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, May 2nd, **1951**, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by Mr. R. C. Chirnside, F.R.I.C., Vice-President.

The following papers were presented and discussed: "The Estimation of Boron in Boronised Metals," by G. H. Bush, B.Sc., A.R.I.C., and D. G. Higgs; "The Determination of Germanium. Part I. Titration of Mannito-Germanic Acid. Part II. Absorptiometric Determination with Phenylfluorone. Part III. Determination in Flue Dust, Coal and Coke," by H. J. Cluley, M.Sc., A.R.I.C.

NEW MEMBERS

Denis Coyle; Alan Leslie Glenn, B.Sc., B.Pharm., Ph.C.; Leslie John Holton; George Norwitz, B.A. (Phil., Pa); Clément Tibi; Albert Frederick Williams, B.Sc. (Lond.), F.R.I.C.

NORTH OF ENGLAND SECTION

AN Ordinary Meeting of the Section was held at the Engineers' Club, Albert Square, Manchester, on Saturday, April 14th, 1951, at 2 p.m. The Chairman of the Section, Mr. A. A. D. Comrie, presided over an attendance of 30. The retiring Chairman, Mr. J. G. Sherratt, delivered his Chairman's Address, which dealt with the comparison between the methylene blue grading test and the plate counts of ice-cream.

SCOTTISH SECTION

AN Ordinary Meeting of the Section was held on Friday, April 20th, 1951, at 7 p.m., in the North British Hotel, Edinburgh. Mr. H. C. Moir presided and 36 members and friends were present.

A lecture entitled "The Microscope as an Analytical Aid" was given by Mr. Gordon Rattray, Ph.C., F.R.M.S.

Addendum* to Report No. 13† of the Essential Oils Sub-Committee of the Analytical Methods Committee

THE DETERMINATION OF ESTERS

THE Analytical Methods Committee has received from the Essential Oils Sub-Committee‡ the following Addendum to their Report No. 13, "The Determination of Esters" (*Analyst*, 1937, **62**, 541), and its publication has been duly authorised.

ADDENDUM

Twenty millilitres of distilled water shall be added to the contents of the flask after saponification and before titration; a similar addition shall be made to the blank. This modification makes the end-point sharper and is particularly helpful for dark-coloured oils.

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* Individual copies of this Addendum will be supplied, without charge, on application.
† *Analyst*, 1937, **62**, 541.
‡ Membership as published in *Analyst*, 1950, **75**, 286.

Inorganic Chromatography on Cellulose

Part IV*

Determination of Inorganic Compounds by Paper-Strip Separation and Polarography

By J. A. LEWIS and J. M. GRIFFITHS

(*Presented at the meeting of the Society on Wednesday, February 7th,* 1951)

Separations are described in which problems of interference in quantitative analysis are overcome by using paper-strip chromatography. These separations can be divided into three types: (*a*) the separation of one individual from a number of metals, (*b*) the separation of a group of metals into individual metal salts and (*c*) the separation of a larger group into smaller groups of metal salts in which interference no longer occurs. Final estimations have been carried out by polarography.

THE separation of inorganic salts by a chromatographic technique using absorbent paper in conjunction with organic solvents has already been the subject of a number of publications from this laboratory.[1,2,3,4,5] The work with paper strips has, however, mainly been concerned with qualitative analysis, although the application of the technique as a basis for quantitative estimation of metals has been indicated. This paper presents details of the separation and determination of a number of metals and mixtures of metal salts by means of chromatography on paper strips followed by polarography for the final determination. The separation[3,4] is performed by placing an accurately measured volume of the test solution near one end of a strip of absorbent paper. The end of the strip nearest the test patch is then immersed in the organic solvent, which is allowed to diffuse through the paper and over the sample of metal salts; one or more of the metal salts dissolve and move down the paper to form well-defined zones. The regions containing the metal salts are then separated from the rest of the paper strip and the amount of metal in each region, after solution, is determined by the polarograph. Three types of separation are described, (*a*) the separation of one metal from a mixture, exemplified by uranium in the presence of a large number of other metals, (*b*) the separation of several metal salts in a mixture, such as cobalt, nickel and copper in a sample of alloy steel and copper and cobalt in iron pyrites and (*c*) the separation of a mixture of metals into groups containing several metals that can be determined by polarography without further separation, represented by ten metals separable into two groups of five containing (*i*) vanadium, copper, uranium, lead and titanium and (*ii*) iron, molybdenum, bismuth, antimony and cadmium.

A new supporting electrolyte for polarography that makes use of salicylic acid to form complex ions with certain metals has been found valuable for determination of several metals in a mixture.

This combination of chromatographic separation and polarography has proved satisfactory, the procedure being both rapid and reasonably accurate when the smallness of the quantities of material required for test is borne in mind. Moreover, the method shows promise of wide application in micro-analytical work.

EXPERIMENTAL

The extension of paper chromatography to a quantitative method required rigorous attention to details, *i.e.*, the acidity of the metal solution, the effects of interfering anions, the composition of the solvent and sometimes of the atmosphere in the gas-jar. Methods for the removal of metals or groups from the paper and subsequent treatment to produce a convenient solution for estimation have been investigated. Volumes were measured on to the paper (Whatman No. 1) with a micrometer syringe.

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* For particulars of earlier papers in this series (not in *The Analyst*), see reference list, p. 395.

THE SEPARATION AND DETERMINATION OF ONE METAL FROM A GROUP OF METALS—

The first type of paper strip separation investigated was the isolation of one element, and the first element so examined was uranium. The isolation of this element on a semi-quantitative basis has been described by Arden, Burstall and Linstead.[3] The solvents used were tetrahydrosylvan and tetrahydropyran with additions of small amounts of nitric acid and saturated with water. For quantitative separation it was found necessary to use at least 5 per cent. of nitric acid with tetrahydrosylvan and at least 7 per cent. of nitric acid with tetrahydropyran. Among simple solvents, nitromethane shows promise of being useful for the separation. The original metal solution was in nitric acid of 50 per cent. v/v concentration.

It was found that the whole of the uranium was always present in the leading 6 cm of the solvent run and that a run of 10 cm was sufficient to separate uranium from the common metals. To test the effects of other metals a run was carried out with trace amounts of the following present: Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, Ce, La, Pr, Ta, W, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th. The effect on the quantitative separation of uranium was negligible. With regard to anions, phosphate can be tolerated in amounts up to 0·7 *M* in the original metal solution provided there is an excess of ferric iron present and provided a run is continued for 16 cm in order to obtain a section of paper sufficiently free from phosphate to be ignited. Sulphate can be tolerated in amounts up to 0·8 *M*. Above these concentrations, phosphate and sulphate cause the uranium to spread over the paper. These high concentrations, however, are unlikely to be encountered in a solution of a sample. Chloride ions promote the movement of other metallic ions, notably iron, on the paper.

A solution of the uranium is made by removing the paper from the gas-jar, drying it, tearing out the last 6 cm of solvent run and burning this section of paper. It was found that heating the paper in a crucible to reduce it to ash led to low results, so the paper is held by one corner in glass forceps and burnt, the ash being dropped into a beaker. The unburnt corner, remote from the leading solvent edge, can be rejected. The ash is then twice taken to dryness with a few drops of diluted perchloric acid, 2 ml of acid (0·1 *N* hydrochloric acid saturated with alkali-soluble methyl cellulose) are added, the whole is stirred with a glass rod and 1 ml of the resulting solution is taken for polarographic estimation between 0 and —0·4 volt.

The results shown in Table I are for synthetic solutions used in the course of a study of the method. With synthetic solutions it was found necessary to add ammonium nitrate to the original solution as "salting-out" agent; this is unnecessary with sample solutions.

TABLE I

DETERMINATION OF U_3O_8 IN SYNTHETIC SOLUTIONS

Quantity of U_3O_8 on absorbent paper, µg ..	20	70	100	150	200
Observed quantities of U_3O_8 determined by polarograph, µg	24	68	101	141	211
	26	68	101	142	193
	24	72	101	142	197
	20	69	99	145	204
	24	72	93	147	201
	21	67	102	147	204
Mean observed quantities of U_3O_8, µg ..	23	69	99	144	202

Solutions of ores and other products have given results of which a selection are shown in Table II. The first five results on siliceous ores have been published by Arden, Burstall and Linstead.[3]

The method has been used with satisfactory results for routine estimations and exemplifies the isolation of one element for analysis.

THE SEPARATION OF A GROUP OF METALS INTO INDIVIDUAL METAL SALTS—

For some groups of metals, estimation in the presence of one another is difficult and the chemical separation tedious. As an example of the application of paper-strip separation to such a group, a mixture of the chlorides of nickel, manganese, cobalt, copper and iron can be separated into individual metal salts and taken into solution for estimation. The polarograph was used for final determination. In simple chloride solution, polarographic estimation presents problems of interference within this group, but the metals, once separated, can be estimated in any desired supporting electrolyte.

For the purpose of the extraction, the atmosphere in the gas-jar was brought to equilibrium with separate vessels, together in the same gas-jar, containing (*a*) saturated ammonium nitrate solution (giving 65 per cent. relative humidity) and (*b*) acetone. The paper strips were allowed time to "condition" in this atmosphere after placing the spot of solution 12 cm from the top of the paper. The solvent used for extraction was 50 parts by volume of acetone, 8 parts of concentrated hydrochloric acid and 42 parts of methyl *n*-propyl ketone, b.p. 98° to 100° C. This solvent was allowed to seep down through the spot for a distance of at least 30 cm. The separation was usually complete in about 6 hours at normal room temperature of about 20° to 25° C. By tapering the upper end of the paper to less than 1 cm to reduce "wick" action and using a strip 40 cm long and 3·5 cm wide, it was possible to allow the run to proceed overnight.

TABLE II

COMPARISON BETWEEN DETERMINATIONS OF URANIUM BY CHEMICAL AND PAPER-STRIP METHODS

	Uranium as U_3O_8 determined by	
Type of ore	Chemical analysis, %	Polarographic analysis, %
Pitchblende	26·46	26·4
Siliceous	1·33	1·25
	1·26	1·16
	0·31	0·30
	0·69	0·70
	0·91	0·94
	0·045	0·050
	1·28	1·53
	0·19	0·21
Monazite	0·37	0·35
	0·34	0·34
	0·38	0·38
Phosphate	0·024	0·039
	0·015	0·020
	0·009	0·011

When the run was completed, the strip was removed and dried and the positions of the various metals ascertained by exposing the strip to strong ammonia vapour and then spraying it with a mixture of equal volumes of rubeanic acid (a 0·25 per cent. solution in alcohol) and 1 per cent. of benzidine in a 10 per cent. aqueous solution of acetic acid. The two stock solutions were mixed just before use. Nickel, manganese, cobalt and copper, under this treatment, give deep blue, pale blue, yellow and greyish-green stains, respectively, which appear in that order down the paper. Iron gives a very pale brown self-colour below all the foregoing metals. The manganese position is marked lightly with pencil as the colour is transient.

The sections of the strip containing the various metals were then cut out and ashed in separate crucibles, the ash being taken just to dryness with the appropriate fuming agent, dissolved in 2 ml of supporting electrolyte and a polarogram taken with the conditions as indicated in Table III. In the fuming process, the use of industrial infra-red lamps over the vessels was found most valuable in avoiding spitting, baking and the necessity for constant supervision.

In Table III mean results found by this procedure are shown, the maximum deviation from the mean being 5 per cent. in the region of 75 to 100 μg; the deviation increases as the amount of metal decreases. For iron, a blank of about 30 μg has been measured on a strip of filter-paper cut adjacent to that on which the estimation was carried out, and this figure has been subtracted from the observed result. Because of this blank with Whatman No. 1 filter-paper, no determination of iron has been made below 30 μg. Filter-papers of lower ash content have been shown to give a lower blank, but do not give quite such good separations.

An alloy steel and a sample of iron pyrites have been analysed for some of these elements by this technique. The alloy steel was digested with aqua regia, taken to dryness several

TABLE III

MEAN RESULTS OF POLAROGRAPHIC DETERMINATIONS BY THE PROCEDURE DESCRIBED

	Ion					
	Nickel	Manganese	Cobalt	Copper	Iron	Remarks
Fuming agent	Hydrochloric acid	Hydrochloric acid	Aqua regia, then hydrochloric acid	Nitric acid	Nitric acid	—
Supporting electrolyte	*N* potassium chloride saturated with alkali-soluble methyl cellulose	0·1 *N* potassium chloride +0·01 per cent. of gelatin	0·1 *N* potassium chloride +0·02 per cent. of agar-agar	10 per cent. sodium potassium tartrate	*M* potassium oxalate	Dissolution of copper is very slow
μg (calc.)	100	100	100	100	100	All from one strip of paper
μg (obs.)	99·5	96	98	97·5	102	
μg (calc.)	75	75	75	75	75	All from one strip of paper
μg (obs.)	75	71	75	76	77	
μg (calc.)	10	10	10	10	30	Each extracted from 100 μg of each of the other metals
μg (obs.)	10	10	12·5	10	33·5	

times with hydrochloric acid and then digested with hydrochloric acid, diluted and filtered. The residue was dissolved in caustic soda and tungstic acid was precipitated by acidifying the solution with hydrochloric acid. The mixture was filtered and the bulked filtrates were made up to 50 ml; 0·10 ml of this solution, representing 2135 μg of sample, was taken for estimation.

The iron pyrites was dissolved in aqua regia, evaporated to dryness and then taken to dryness several times with, and finally dissolved in, hydrochloric acid. The solution was made up to 25 ml, and 0·05 ml, representing 4956 μg of sample, was taken for estimation.

Both experiments were performed in quadruplicate with the results shown in Table IV.

TABLE IV

ANALYSES FOR COBALT, NICKEL AND COPPER IN AN ALLOY STEEL AND A SAMPLE OF IRON PYRITES

Element in alloy steel	Amount present as stated by the British Chemical Standards, %	Found, %	Remarks
Cobalt	4·35 (4·26 to 4·46)	4·40	
Nickel	0·43 (0·42 to 0·47)	0·45	
Copper	0·05 approx.	0·04 approx.	By comparison of standard stains
Element in iron pyrites	Amount present as stated by Bureau of Analysed Samples, Ltd., %	Found, %	Remarks
Copper	2·69	2·70	
Cobalt	0·10	0·12	Cobalt section taken up in base containing some cobalt*
Nickel	Trace (one observer)	Trace	Rubeanic acid stain

* This was found to aid consistent results for the very small amount of cobalt on the paper.

Notes—Technical grades of methyl *n*-propyl ketone were tested for discolouration with concentrated hydrochloric acid and grades that did not discolour were chosen for this work. The ketone as obtained was distilled and the fraction boiling in the range 98° to 100° C was used.

Occasional cleaning and recharging of gas-jars is advisable for the maintenance of good results.

The elements gallium, zinc and uranium, which tend to interfere with the polarographic estimation of nickel and cobalt in chloride solution, move into the copper - iron region on the paper strip and do not interfere with the estimation of these in their respective supporting electrolytes.

The effect on the separation of anions other than chloride has been examined, and it was found that up to 20 per cent. of nitric acid or calcium nitrate and 10 per cent. of sulphuric acid or sodium sulphate (in the original metal solution) could be tolerated. Above these limits, the separations were progressively less satisfactory.

THE SEPARATION OF A GROUP OF METALS INTO SMALLER GROUPS—

In the course of a search for supporting electrolytes of wide application to the polarographic determination of metals, salicylic acid in aqueous solution was found to be valuable in giving well-defined waves at convenient intervals for certain metals. This supporting electrolyte can be used, for example, in the estimation of commonly occurring groups of metals, such as (*a*) vanadium, molybdenum and titanium, (*b*) iron, copper and uranium and (*c*) bismuth, antimony and lead, in one operation. Other possible combinations can be derived from Table V on p. 394.

During the investigation of this supporting electrolyte containing salicylic acid, it was found that iron interfered with vanadium, molybdenum and bismuth with copper, antimony with uranium, and titanium with cadmium. A simple paper-strip separation was therefore used to divide these metals into two groups in which each metal could be directly estimated. Investigation showed that *n*-butyl alcohol in conjunction with hydrochloric acid* separated the chlorides of these ten elements into two groups within which all interference was eliminated. The promise shown by the early work was mentioned by Burstall, Davies, Linstead and Wells[4] in Part II of this series, but some modification has since been made to render the separation quantitative.

Molybdenum is estimated after conversion on the paper strip to molybdenum blue, which reduces at a potential less negative than does molybdic acid. This fortunate discovery was useful in that the half-wave potential was thereby separated from that of bismuth in the same sub-group.

SALICYLIC ACID AS A SUPPORTING ELECTROLYTE FOR POLAROGRAPHY

Among a number of organic acids, salicylic acid showed promise of being useful in complexing certain metals so that waves were produced on the polarograph at convenient intervals. The satisfactory use of salicylic acid appears to depend on the following factors—

(*a*) Salicylic acid concentration is not critical, but 1 volume of saturated solution in 4 volumes of final solution gives good results.

(*b*) Sulphuric acid (about 5 per cent. v/v) should be present so that the pH of the final solution is less than 2.

(*c*) Chloride ions should be absent. The presence of chloride alters the anode potential and prevents the appearance of waves for vanadium, iron and molybdenum blue at the start of the polarogram. If these metals are to be estimated, chloride can be removed by shaking the solution with solid mercurous sulphate and then filtering it, although an allowance must be made for a mercurous wave at 0 volts.

(*d*) Phosphate ions should be absent. The presence of this anion causes coalescence of polarographic waves in salicylic acid.

(*e*) Nitrate must be absent. In acid solution, attack on the anode by any appreciable amount of nitrate ion renders zero setting difficult and vitiates readings for iron and vanadium. It also has a slight effect on wave heights generally.

(*f*) Alizarin may be present with advantage. A small amount of solid AnalaR alizarin, added to the final solution, prevents the appearance of maxima, *e.g.*, on the copper wave. After a paper-strip separation, this addition of alizarin is not necessary, probably because the maxima are suppressed by cellulose dissolved when the metals are taken into solution for polarography.

Routine estimations of iron have been performed with satisfactory results, in the absence of vanadium, by adding 1 volume of solution in sulphuric acid to 1 volume of an aqueous solution comprised of—

Half-saturated salicylic acid.
Half-saturated A.R. alizarin.
10 per cent. v/v concentrated sulphuric acid, A.R., sp.gr. 1·84.

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* Solvent suggested by Mr. N. F. Kember of this laboratory.

A procedure found satisfactory for evaluation of waves in the region of zero e.m.f. (*e.g.*, that for iron) is to measure wave heights from a line obtained by polarography of the supporting electrolyte only, before the metal solution is added.

The other nine elements can be estimated to an accuracy of ±3 per cent. (±1 per cent. for copper) in concentrations of 30 to 1500 μg per ml in the final solution, estimations being made in triplicate. Between 5 and 30 μg per ml the accuracy of the determinations decreases to ±20 per cent. Other common cations with the exception of tin do not interfere.

PAPER-STRIP SEPARATION TO ELIMINATE INTERFERENCE

Solutions were made up to contain the chlorides of copper, uranium, lead, iron, bismuth, antimony and cadmium together with titanium hydroxide (precipitated from sulphate) and ammonium vanadate and molybdate. The best separations in the initial experiments were attained with 20 per cent. of hydrochloric acid in the aqueous solution of metal salts, with the spot left wet on the paper, and with 5 per cent. v/v of concentrated hydrochloric acid in the butyl alcohol used as separating solvent. These conditions were therefore used in all subsequent investigations. Separations have been made on Whatman Nos. 1 and 3 filter-papers. The former gives a slower run of about 9 hours or, conveniently, overnight and will take a maximum of 0·1 ml of solution on a strip 2·5 cm wide. The No. 3 paper permits separation in 3 hours and 0·25 ml of solution can be taken up on the paper without impairing results.

The groups into which the metals separate are: (*a*) vanadium, copper, uranium, lead and titanium in the upper section of the paper; (*b*) iron, molybdenum, bismuth, antimony and cadmium in the lower quarter of the solvent run.

There is a metal-free space between these two groups which facilitates division. The line at which to part the paper is detected by producing molybdenum blue on the strip. This is visible only when at least 100 μg of molybdenum is present. With smaller amounts, the leading quarter of the solvent run is assumed to contain group (*b*); alternatively, a known amount of molybdenum is added to the sample solution. The colour of the reduced molybdenum compound is developed by drying the strip under an infra-red lamp, followed by spraying with a saturated aqueous solution of butyl alcohol and again drying. The strip is then exposed simultaneously to air and the vapour from dilute ammonia. Infra-red radiation or sunlight and a pH of about 4·0 appear to be essential to the production of the colour. Should the colour appear before completion of the treatment, the treatment is discontinued. The strip is torn immediately above the blue spot and the metals are extracted for polarography.

Some trouble was experienced in removing the groups quantitatively from the paper before the polarographic determination. The methods tried were (*i*) ashing, (*ii*) macerating with cold acid and (*iii*) digestion with hot acid. A limitation was imposed by the requirements for the final solution. The procedure finally adopted was to boil the section of the paper concerned for 1 minute, first with water, then with saturated aqueous salicylic acid, and then to heat with 2 *N* sulphuric acid. The last stage had the effect of pulping the paper, which was then filtered through sintered glass, together with added mercurous sulphate (see later) before adding the filtrate to the other extracts. It was also found necessary to cool the solutions before combining them in order to avoid decomposition of molybdenum blue. Chloride was removed from the combined water and salicylic acid extracts before adding the chloride-stripped sulphuric acid leach. Removal of chloride was achieved by shaking with a small amount of solid mercurous sulphate, 1 drop of which was added as a slurry with dilute sulphuric acid; the solution was then filtered through sintered glass, conveniently from a Schwarz - Bergkampf micro-beaker, into the sulphuric acid filtrate. On subsequent polarographic estimation, a mercury wave is produced at 0 volts, and a correction must be made when estimating vanadium or iron.

THE EFFECT OF VARIOUS IONS ON THE SEPARATION

Most common cations, tin being an exception, do not give waves in the salicylic acid medium and hence do not interfere in these determinations. Tin, however, prevents the development of molybdenum blue in the paper separation and also interferes by interaction with ferric iron. In addition, tin gives a wave that interferes with cadmium, but only if present in excess of the equivalent of any ferric iron that is present.

Phosphate ions interfere with the paper-strip separation when present in concentrations above the equivalent of 0·03 M orthophosphoric acid in the sample solution. Phosphate also inhibits the formation of the molybdenum blue compound.

Sulphuric acid in the sample solution can be tolerated up to 0·2 M, but interferes with the development of the molybdenum blue colour and slows down the movement of the metals in relation to that of the solvent front on the paper strip.

Where phosphate or sulphate, or both, are present, two paper strips are run in parallel. One is then developed with potassium ferrocyanide to find the position of the molybdenum, which shows up as a dull brown stain. The other strip is then assumed to have the molybdenum in a corresponding position and is divided above this to give the two groups for estimation.

HALF-WAVE POTENTIALS IN SALICYLIC ACID

The half-wave potentials of the elements, determined after the separation and solution procedures already described, are given in Table V. These potentials are determined against an internal mercury anode.

TABLE V

HALF-WAVE POTENTIALS IN SALICYLIC - SULPHURIC ACID

Element	$E_{\frac{1}{2}}$, volts	Group
Vanadium	−0·025	Upper section of filter-paper
Copper	−0·375	
Uranium	−0·575	
Lead	−0·725	
Titanium	−1·025	
Iron	−0·025	Lower section of filter-paper
Molybdenum blue	−0·20	
Bismuth	−0·40	
Antimony	−0·60	
Cadmium	−1·125	

RESULTS

The quantities that can be estimated by the combined paper-strip - polarograph method are limited (*a*) by the amount of the metal chlorides that will dissolve in 0·25 ml of solution and (*b*) by the amounts that can be quantitatively removed from the paper and estimated on the polarograph.

TABLE VI

QUANTITATIVE RESULTS

Observed amount					
Vanadium, µg	Copper, µg	Uranium, µg	Lead, µg	Titanium, µg	Calculated amount, µg
995	1000	985	960	960	1000
96	102	97	97	92	100
28	29	29	30	29	30

Ferric iron, µg	Molybdenum, µg	Bismuth, µg	Antimony, µg	Cadmium, µg	Calculated amount, µg
965	955	1020	1035	960	1000
94	99	100	104	98	100
27	28	31·5	31	30·5	30

For routine work, preliminary experiments indicate that the use of the method of standard addition for one element can be followed by the use of that element as internal standard for the others. Disproportionate amounts can easily be separated and can be estimated within the usual limits of polarography, *i.e.*, a small wave for a metal can be estimated accurately when it occurs before, but not after, a large one. Means of three results are quoted in Table VI; the maximum deviations from the mean were 6 per cent. in the 1000-µg range and in the 100-µg range, becoming progressively greater as the amount of the metals decreased. The determinations were carried out by comparison with standard wave heights. Each measurement was made in the presence of a similar concentration of the other nine elements.

A standard mercury wave height has been subtracted from the values for iron and vanadium. The solubility of lead in sulphuric acid is greatly increased by the prior addition of salicylic acid. The lead wave is always small, and it has been found that the use of a nearly neutral nitrate solution instead of sulphate is advisable where the estimation of lead is important. The original chloride solution of titanium must be freshly prepared to avoid hydrolysis. The tendency for high results to be obtained for bismuth and antimony may be due to molybdic acid regenerated by the ferric iron, and the estimation of this group must be carried out quickly after the metals have been removed from the paper.

The polarograph has been shown to be a useful instrument for the final estimation of quantities separated by paper-strip extraction, and conversely the extractions are considered a valuable complement to polarography by extending the scope of the technique.

These investigations have been carried out in part for the Ministry of Supply and in part for the Chemistry Research Board, D.S.I.R., and are published by permission of the Director of the Chemical Research Laboratory.

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NOTE—References 3, 4 and 5 are to Parts I, II and III of this series.

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Discussion

DR. H. LIEBMANN asked whether R_F values individually determined were a reliable guide to the possibility of separating a given metal from others, and if the presence of other metals influenced the R_F values.

MR. LEWIS replied that, while other metals had some effect on the movement of a particular element, the R_F value individually determined was a very strong indication of its behaviour in other circumstances. Anions, however, had great effects on R_F values.

MR. D. G. HIGGS asked whether it was possible to separate very small quantities of metals such as iron from relatively pure metals such as molybdenum. Would it be possible, for example, to separate 0·01 per cent. of iron from more than 99·5 per cent. pure molybdenum?

MR. LEWIS answered that the problem of separating trace amounts (and parts per million could be successfully dealt with) was best solved by the use of upward development on a paper cone. A large amount of sample could be put on the paper around the base and the solvent chosen so that the trace element was concentrated at the apex.

DR. J. H. HAMENCE asked the authors whether from their very wide experience of inorganic chromatography they could give an opinion as to the best technique to apply in developing a chromatograph. Various workers had used different techniques, some with the paper in a vertical and others with it in a horizontal position. Which did the authors consider to be the better?

MR. LEWIS said that the workers at the Chemical Research Laboratory had found downward displacement the best technique in most circumstances and held that the assistance of gravity was useful.

MR. J. HASLAM asked whether, in the determination of the general metal content of foodstuffs after a preliminary wet digestion, it was likely that addition of salicylic acid and subsequent polarography of the wet digestion product would give a useful general picture of the metal content of the foodstuff.

MR. LEWIS replied that the salicylic acid supporting electrolyte would undoubtedly be useful for the estimation of small amounts of lead, antimony or copper in a sulphuric acid digestion product, but that the commonly occurring tin might cause complications.

DR. LIEBMANN asked whether tin produced a curve in the salicylic acid medium, and if so, which metals would interfere.

MR. LEWIS said that tin did produce an ill-defined wave in salicylic - sulphuric acid at 1·1 volts, where it interfered with cadmium, but only if present in excess of its equivalent of ferric iron. It interfered with iron by reducing it, and was itself oxidised.

MR. N. STRAFFORD asked whether arsenic would give a wave in the determination of poisonous metals in foodstuffs, medicinals, and so on, by polarography. If it did not, then polarography would not provide a universal method for the determination of poisonous metals.

MR. LEWIS stated that arsenic did not give a wave in the salicylic medium, but that useful waves had been reported in other media. In a limited experience of this particular element, he had not found a wave suitable for analysis.

Inorganic Chromatography on Cellulose

Part V

The Use of Columns of Cellulose in Combination with Organic Solvent Extraction for the Separation of Uranium from Other Metals

BY F. H. BURSTALL AND R. A. WELLS

(Presented at the meeting of the Society on Wednesday, February 7th, 1951)

A new method is described for the separation of uranium from other metals; it is based on the extraction of uranyl nitrate with ether containing 5 per cent. v/v of nitric acid in the presence of cellulose. The method has been applied to the determination of uranium in minerals and ores with results that compare favourably in simplicity, rapidity and accuracy with other methods. The behaviour of a number of other anions and cations in the process has been investigated and methods have been devised for overcoming difficulties caused by the presence of some metals and acid materials on the extraction process.

IT has been known for many years that uranyl nitrate is soluble in ether and other organic solvents, and this fact has been widely used as a basis for the separation of uranium for the determination of the element in minerals, ores and other products. The method, however, does not always give a pure extract of uranyl nitrate and further treatment is necessary. In early work with paper strips and organic solvents containing nitric acid, Arden, Burstall and Linstead[1] found that very good separations of uranium from a large number of other metals could be achieved. The use of paper strips limits the quantity of material that can be used, but in later work by Burstall, Davies and Wells[2] it was found possible to separate much larger quantities of metallic products by using columns of cellulose pulp packed in organic solvents and contained in glass tubes, and the application to uranium was briefly indicated. A detailed account is now given of the use of ethyl ether containing 5 per cent. v/v of nitric acid as solvent and cellulose pulp as adsorbent, for the quantitative extraction of uranium from a variety of materials. The method consists in preparing a nitrate solution of the sample for analysis in dilute nitric acid and transferring this mixture to the top of a column packed with cellulose in the presence of the ethyl ether - nitric acid solvent. The solvent is allowed to percolate through the column; uranyl nitrate is dissolved and passes quantitatively into the liquid eluent, whereas a larger number of other metals remain stationary or move only slowly in comparison with uranium. The uranyl nitrate is readily recovered from the eluent after it has been diluted with water and the solvent removed by distillation; the uranium can be determined by gravimetric, volumetric, colorimetric, polarographic or fluorimetric techniques.

The method has proved widely applicable in the separation of uranium from minerals, ores and other products. The procedure is simple and rapid and has given results comparable in accuracy with those of other methods.

The mechanism of the separation process is complicated and is dependent chiefly on the following factors—

(*a*) *Selective extraction of uranyl nitrate by the solvent*—Nitrates of metals other than uranium (*e.g.*, ceric, ferric, mercuric and thorium nitrates) also dissolve in ether, but under the conditions of the extraction these metal salts are retained by the cellulose. Ceric nitrate is reduced to the cerous condition and is then retained, mercuric nitrate is also retained by the cellulose, and movement of ferric and thorium nitrates depends largely on the amount of water present in the system. The solubilities of metal nitrates are substantially dependent on the concentration of nitric acid in the solvent, an increase in nitric acid concentration causing an increase in solubility. The use of 5 per cent. v/v of nitric acid in ethyl ether for the extraction of uranium has been found most satisfactory for analytical work; it provided a suitably pure uranyl nitrate with a small amount of solvent.

(*b*) *Partition between the nitrates dissolved in the organic solvent and water present in the cellulose*—This is also important; indeed, water is a key factor in chromatography with organic solvents and solid adsorbents.

(*c*) *Adsorption of metals on the cellulose*—This also plays a part in the separation. Uranyl nitrate in ethyl ether containing 5 per cent. v/v of nitric acid is not adsorbed although many other metals are strongly retained on the cellulose. This chemical adsorption is due to the presence of reactive groups in the cellulose, and can be increased by pre-treatment such as boiling the cellulose with dilute nitric acid.

The foregoing factors are still being investigated in order to gain further details of the mechanism of chromatographic separation, but lack of information on this aspect of the process does not affect the value of the experimental technique in the analysis of uranium.

EXPERIMENTAL

SOLVENT PREPARATION AND RECOVERY—

The solvent was freshly prepared each day by mixing ethyl ether, free from peroxide, with concentrated nitric acid, sp.gr. 1·42, in the proportion of 5 ml of acid to 100 ml of ether. The ether was recovered by addition of water followed by distillation and purified for re-use by neutralisation with caustic soda, treatment with alkaline permanganate, distillation, drying over caustic soda and a final fractionation. Each batch of ether was tested for peroxide with potassium iodide solution before use. Estimations by the Fischer method indicated that the water content was less than 0·1 per cent.

PREPARATION OF CELLULOSE—

The cellulose pulp was prepared by boiling 450 g of cellulose (Whatman Ashless Tablets) with 3 litres of 5 per cent. v/v nitric acid for 2 minutes. Other forms of cellulose can be used, for example, Whatman No. 1 Waste Paper Clippings, which require boiling for 20 minutes, however. The pulp is filtered and washed free from nitric acid with water and then washed with 2 litres of ethyl alcohol and finally with about 2 litres of ether. After draining at a filter-pump, the pulp is stored in a closed container and is ready for use. Experiments were carried out to ascertain the amount of inorganic impurities extractable from a column of cellulose pulp, 2 cm in diameter and 25 cm long, by the mixed ether - nitric acid solvent. As shown in Table I, the pulp made from No. 1 clippings is sufficiently pure for most purposes provided that the column is first washed through with 250 ml of solvent.

TABLE I

INORGANIC MATERIAL EXTRACTABLE FROM CELLULOSE

Source of pulp		Volume of ether - nitric acid mixture passed through 25-cm column, ml	Weight of ignited residue from eluent, g
Ashless tablets		250	0·0000
No. 1 clippings	1st	250	0·0008
	2nd	250	0·0001

THE EXTRACTION TUBE—

The adsorption apparatus consists of a glass tube about 2 cm in diameter and 40 cm long, the upper end being widened to form a funnel to allow easy transfer of material to the tube. The lower end of the tube is narrowed and is closed by a short length of polyvinyl chloride tubing carrying a screw clip or a tap. The inside surface of the glass extraction tube was treated with dichlorodimethyl silane, $(CH_3)_2SiCl_2$, which conferred strong water-repellent properties to the glass surface (see Burstall, Davies and Wells,[2] Part III of this series, p. 180). Another method of achieving water-repellent properties was to use Fluid 200 (Albright and Wilson Ltd.) in carbon tetrachloride solution; with this, the tube must be heated to 250° C to provide a stable water-repellent film. The adsorption tube was packed with cellulose pulp in the following way. The tube was first half-filled with ether - nitric acid mixture and cellulose pulp was added in small quantities. Each portion of pulp was gently pushed down with a glass rod flattened at one end to form a plunger of diameter slightly less than that of the tube; a brisk up and down movement of the plunger then served to break up any aggregated pieces of pulp. A column properly packed in this way allowed ether solution to pass freely through the cellulose at a rate of approximately 100 ml in 20 minutes with the end of the tube completely open. Cellulose columns from 5 to 8 cm in length were ultimately used, but initial experiments were made with 25-cm columns.

PREPARATION AND TRANSFER OF SAMPLE—

A solution of the sample was prepared in aqueous nitric acid. Use of a high concentration of nitric acid favoured the rapid extraction of uranium in a narrow band. The movement of many impurities, however, decreased with the concentration of the nitric acid. A suitable compromise was found to be a solution containing 25 per cent. v/v of nitric acid. The method of preparing a nitric acid solution of the sample varied with the type of mineral, and is described later separately for each type of ore, together with any special treatment of the solution found necessary.

The acid solution of the sample could be transferred directly to the top of the column, but the following method was usually adopted. Sufficient cellulose pulp was added to the sample solution to ensure complete adsorption; the amount required was 2 g of pulp for 10 ml of 25 per cent. v/v nitric acid. This wad of cellulose was then transferred to the top of the tube, gently beaten with a plunger and pressed down to form a continuous part of the column.

THE EXTRACTION OF URANIUM—

After transfer of the sample, successive small volumes (10 ml) of the ether containing 5 per cent. v/v of nitric acid were added and the solvent was allowed to flow through the tube. This procedure was continued until 150 ml of solvent eluent had been collected, this quantity being adequate for an 8-cm cellulose column, although proportionately larger quantities must be used with longer columns. The solvent was added in such a manner that the level of the solvent at the top of the column fell to the top of the cellulose packing, but not below, between successive additions. The extraction column was not allowed to run dry at any stage. To the eluent from the extraction was added water in the proportion of 50 ml of water to each 100 ml of solvent and the ether was removed by distillation. The uranium was then determined by one of the following methods: (*a*) evaporation and ignition to U_3O_8; (*b*) precipitation with oxine, filtration and ignition to U_3O_8; (*c*) evaporation with sulphuric acid and heating to fumes followed by dilution, reduction in a Jones reductor and titration with ceric sulphate; (*d*) evaporation with sulphuric acid and heating to fumes followed by a colorimetric estimation with alkaline solution and hydrogen peroxide; (*e*) as method (*d*) but with a polarographic determination in place of the colorimetric method.

THE BEHAVIOUR OF ELEMENTS OTHER THAN URANIUM—

A study has been made of the behaviour on a cellulose column of other elements under the conditions used for uranium extraction and of the effect of these elements on the extraction of uranium. The following observations are based on a preliminary study. A more detailed account will be given in a further paper.

The nitrates of Li, Na, K, Cs, Rb, Cu, Ag, Be, Mg, Ca, Sr, Ba, Ra, Zn, Cd, Al, Y, La, Ce, Pr, Nd, Sm, Eu, Ho, Er, Ga, In, Tl, Ti, Hf, Ge, Sn, Pb, Nb, Ta, Cr, W, Te, Mn, Fe, Co and Ni all remained stationary or moved only very slightly. These metals, therefore, do not interfere with the estimation of uranium. The remaining elments are dealt with separately.

Gold—The dilute solution of gold prepared by the action of nitric acid on gold metal was partly reduced by the cellulose of the column and gave a purple tint to the absorbent. There was also a tendency for colloidal gold to pass through the column. Prior reduction of the gold by treatment of the sample solution with ferrous sulphate resulted in its complete retention at the top of the extraction column. In presence of chloride, gold was extracted readily from the column.

Mercury—Mercury was found to move only in the mercuric state and then not sufficiently rapidly to affect the estimation of uranium. Mercuric salts are partly reduced by the ether - nitric acid solvent in presence of cellulose, and this aided the retention of mercury. A solution of 0·5 g of mercuric nitrate in 5 ml of 25 per cent. v/v nitric acid was extracted with ether containing 5 per cent. v/v of nitric acid through a 10-cm cellulose column. After the passage of 200 ml of solvent, mercury was detected 3 cm from the bottom of the column, but not in the eluent.

Selenium, arsenic, antimony and bismuth—Selenium, arsenic, antimony and bismuth in a column all moved, but not at sufficient speed to be extracted with uranium. For example, bismuth nitrate had moved only 5 cm down a column after the passage of 200 ml of ether containing 5 per cent. v/v of nitric acid. The effect of large amounts of arsenic on the extraction of uranium will be dealt with in a later paper.

Cerium—Ceric nitrate is appreciably soluble in ether - nitric acid mixtures; in addition, its coefficient of partition between ether - nitric acid mixtures and water is high. Since ceric nitrate is absorbed by cellulose from ethereal solutions to a small extent only, steps must be taken to ensure that any cerium is reduced to the cerous state, in which form it is insoluble in most organic solvents. Reduction of ceric nitrate takes place in ether solution in the dark and in the absence of added acid, but the process is slow. For the extraction of uranium from monazite sands, ferrous sulphate was first added to reduce cerium, but a better method was to boil the original solution in dilute nitric acid with hydrogen peroxide.

Thorium—Thorium was extracted in small amounts with ether containing 5 per cent. v/v of nitric acid, but the extraction was very sensitive to the concentration of acid in the solvent. The use of ether containing 3 per cent. v/v of nitric acid permitted uranium to be extracted completely before thorium was detected in the eluent, as shown in Table II.

TABLE II

EXTRACTION OF THORIUM

Nitric acid in solvent, %	Length of column, cm	Weight of ThO_2 in test solution, g	Volume of test solution (in 40% HNO_3), ml	Weight of ThO_2 extracted with 400 ml of solvent, g
3	15	0·450	5	nil
5	25	1·027	10	0·170

When uranium is present as phosphate, as in monazite sands, special conditions must be observed for its extraction; this is referred to later.

Zirconium—Zirconium was also extracted by ether containing nitric acid. Table III shows the results of an extraction of a solution of zirconyl nitrate containing the equivalent of 0·19 g of ZrO_2 dissolved in 3 ml of water and 2 ml of nitric acid, sp.gr. 1·42, when ether containing 5 per cent. v/v of nitric acid was used as solvent. The extraction of zirconium was inhibited by the presence of a number of anions, *e.g.*, phosphate, sulphate, oxalate and tartrate. The use of tartrate for retention of zirconium in the analysis for uranium in zircon-bearing minerals is mentioned later in this paper.

TABLE III

EXTRACTION OF ZIRCONIUM

	Fraction of eluent				
	1st 200 ml	2nd 200 ml	3rd 200 ml	Total 600 ml	Proportion extracted, %
Weight of ZrO_2 extracted ..	0·8 mg	26·0 mg	30·4 mg	57·2 mg	31

Scandium—The behaviour of scandium was similar to that of thorium. The movement of scandium can be inhibited by the addition of tartrate.

Tin—In nitric acid tin is precipitated as insoluble meta-stannic acid, which does not move in the column. But in order to avoid the risk of occlusion of uranium when dealing with minerals containing large amounts of tin, it is best to remove the tin by volatilisation as the iodide. In presence of chloride, tin was extracted very readily from a cellulose column.

Vanadium—Vanadium was immobile in a cellulose column provided that the ethereal solvent used is free from peroxides. In the presence of ether peroxides, a pink peroxy-vanadium compound was formed and moved rapidly down the column. The presence of reducing agents such as ferrous sulphate in the column converted the pink compound to a non-moving vanadium salt.

Phosphorus—Phosphoric acid was readily extracted from cellulose by ether - nitric acid mixtures. In combination with metallic radicals, however, phosphoric acid was much more strongly retained; ferric nitrate has been found a particularly useful complexing agent for this purpose. A small amount of the acid, presumably resulting from the dissociation of ferric phosphate, was, however, still extracted in trace amounts. The presence of a trap of freshly prepared meta-stannic acid in the column reduced the amount of extracted phosphoric acid further, but trace amounts were still detectable in the eluent.

The presence of phosphoric acid inhibited the extraction of uranium, but addition of ferric nitrate overcame this effect.

Molybdenum—The behaviour of molybdenum in cellulose columns appears to vary with a number of factors. When added as a dilute nitric acid solution of ammonium molybdate to a cellulose column and extracted with an ether - nitric acid solvent, the bulk of the molybdenum moved only slightly, but a low concentration of molybdenum was detectable in the eluent. In sunlight there was a strong tendency for molybdenum to be reduced to molybdenum blue and this reaction was catalysed by the presence of uranium. There are indications that there are two forms of the blue complex, one of which was almost immobile and another that was readily extracted from the column. There is also some evidence to show that in concentrated solutions a molybdenum - uranium complex is formed. This behaviour results in a small but definite quantity of molybdenum being present in uranium oxide samples extracted from molybdenum-bearing ores. The proportion of molybdenum in twenty such samples of oxide varied between 7 and 200 p.p.m. Although small, these quantities of molybdenum interfered with the volumetric estimation of uranium by catalysing the aerial re-oxidation of $U^{\cdot\cdot\cdot\cdot}$ to $UO_2^{\cdot\cdot}$ ions. Decrease in the concentration of nitric acid in the solvent or in the aqueous test solution showed little effect. Similarly, carrying out the extraction in the absence of sunlight gave no improvement. It was found that molybdenum could be reduced to an insoluble trioxide by standing it overnight with an excess of ferrous sulphate. The large excess of ferrous sulphate required, however, made this method inconvenient, and other methods, which have been more successful, will be described in a further paper.

The platinum metals—Of the six platinum metals, osmium was neglected, since once it is in solution it is removed by evaporation with nitric acid. Iridium and rhodium were not extracted and hence gave no trouble. Platinum, palladium and ruthenium behave differently.

Ruthenium was fused with potassium hydroxide and a solution of the melt was acidified with nitric acid. The resulting suspension of ruthenium hydroxide was absorbed on cellulose and treated with ether - nitric acid solvent. The ruthenium appeared to be completely retained at the top of the column, but traces were found in the ethereal eluent. Platinum behaved in a similar manner to ruthenium, the main bulk of the platinum being retained at the top of the column, although small quantities were extracted. Palladium in nitric acid solution was readily extracted from a cellulose column. Reduction of the platinum and palladium solutions with ferrous sulphate before extraction was only partly successful in overcoming this difficulty. The bulk of the palladium was retained, but traces of platinum and palladium were still found in the eluent.

Sulphate—Small quantities of sulphuric acid do not appear to have any appreciable effect on the extraction of uranium, but this question has been the subject of a fuller investigation that will be described in a later paper. Free sulphuric acid under normal conditions was retained at the top of the cellulose column.

Halides—Halide ions must be absent from samples used for the estimation of uranium since extraction of other elements is greatly increased. Under normal conditions hydrochloric acid is retained in the column. Both hydrobromic acid and free bromine move slowly down the extraction column. Hydriodic acid and iodine behave similarly.

RESULTS—

Initial experiments were made with nitrate solutions prepared from weighed quantities of pure U_3O_8 with and without added impurities. With a 25-cm column of cellulose, 250 ml of ether - nitric acid solvent were necessary for the complete extraction of uranium, in the absence of phosphate, as shown in Table IV. The presence of phosphate slowed the rate of extraction of uranium considerably, but the addition of ferric nitrate complexed phosphate sufficiently to allow uranium extraction to proceed normally.

TABLE IV

EXTRACTION OF URANIUM FROM SYNTHETIC MIXTURES

Elements present	Weight of U_3O_8 taken, g	Weight of U_3O_8 found, g	U_3O_8 found, %
Uranium	0·0975	0·0970	99·5
Uranium	0·9992	0·9960	99·7
Uranium	0·1721	0·1721	100·0
Uranium + 0·3 g of $Fe(NO_3)_3$	0·0808	0·0808	100·0
Uranium + 0·2 g of each of Fe, Zn, Mn, Cr, V and Cu nitrates	1·0053	1·0043	99·9

APPLICATION TO ANALYSIS OF SILICEOUS MATERIALS

The method was then applied to a number of low-grade siliceous materials. These were all ores that could be dissolved completely by the action of nitric and hydrofluoric acids. Fluoride was removed from the test solution by repeated evaporations with concentrated nitric acid and the residue was finally dissolved in 10 ml of 25 per cent. v/v nitric acid. The weight of sample taken for analysis varied between 0·5 and 5 g; in Table V results are compared with those found by standard methods of chemical analysis.

TABLE V

EXTRACTION OF URANIUM FROM SILICEOUS ORES ON 25-CM COLUMNS

Sample	U_3O_8 by cellulose column %	U_3O_8 by standard chemical methods[3,4] (mean value), %
1	0·36	0·35
2	0·29	0·28
3	0·20	0·19
4	0·20	0·22
5	0·36	0·36
6	0·17	0·16
7	0·38	0·39
8	1·39	1·41
9	0·77	0·73
10	5·03	4·98

The effect of decreasing the column length was then investigated and results with a 5-cm column of cellulose are shown in Table VI. It will be observed that for some estimations the amount of solvent used was only 75 ml. Further experiments (Table VII) in which known weights of uranium oxide were added to a standard ore indicated that results were slightly low when 70 ml of extracting solvent were used; 100 ml were used, therefore, in further experiments.

TABLE VI

EXTRACTION OF URANIUM FROM SILICEOUS ORES ON 5-CM COLUMNS

Sample	Weight of sample, g	Volume of ether, ml	U_3O_8 by cellulose column, %	U_3O_8 by standard chemical methods[3,4] (mean value), %
10	0·5670	250	4·92	4·98
10	0·5019	165	4·95	
10	2·5024	100	5·02	
10	0·5180	75	4·96	
11	2·7869	100	2·15	2·13
11	2·5933	100	2·10	
11	2·4818	100	2·19	
11	2·2242	100	2·15	

Although the results shown in Table VI were considered satisfactory, the ores used in these experiments contained neither vanadium or molybdenum. In view of the tendency for small amounts of molybdenum to be extracted and because of the possible formation of a solvent-soluble peroxy-compound of vanadium with traces of ether peroxides, further analyses were carried out in which small quantities of vanadium and molybdenum were added. The results, as shown in Table VIII, were not unsatisfactory, but during these estimations it was noted that vanadium moved rapidly as a pink band and had usually reached the bottom of the column before 100 ml of ether had passed through the column. Movement of molybdenum under the same conditions appeared to be slight. Addition of ferrous sulphate to the dilute nitric acid solution of the ore maintained the vanadium in a reduced immobile form and did not interfere with the extraction of uranium (Table IX).

TABLE VII

EXTRACTION OF URANIUM ADDED TO SILICEOUS ORES

Weight of U_3O_8 added, mg	Weight of vanadium added, mg	Volume of ether used, ml	Weight of U_3O_8 found, mg
20	10	70	19·85
20	3	80	19·99
20	10	80	19·91

TABLE VIII

THE EFFECT OF VANADIUM AND MOLYBDENUM ON THE EXTRACTION OF URANIUM

Sample	Weight of sample, g	Volume of ether used, ml	Molybdenum added, mg	Vanadium added, mg	U_3O_8 found by cellulose column, %	U_3O_8 found by standard chemical methods^{3,4} (mean value), %
10	0·9665	80	nil	5	4·95	4·98
11	2·5000	100	25	25	2·08	2·13
11	2·4494	100	nil	25	2·17	2·13
11	2·5012	100	25	nil	2·07	2·13
12	3·0526	80	nil	5	0·63	0·66
12	2·4996	100	25	25	0·66	0·66
13	2·4994	100	25	25	0·54	0·54

TABLE IX

EXTRACTION OF URANIUM AFTER ADDITION OF FERROUS SULPHATE

Sample	Molybdenum added, mg	Vanadium added, mg	U_3O_8 found by cellulose column, %	U_3O_8 found by standard chemical methods^{3,4} (mean value), %
11	25	25	2·13	2·13
11	nil	25	2·13	2·13
11	25	nil	2·15	2·13

If the strength of the nitric acid in the test solution was allowed to fall there was a tendency for molybdenum to be reduced to a mobile molybdenum blue by ferrous sulphate. In view of this and because of the undesirability of adding solid material to the original solution, further experiments were made in which the column length was increased to 7·5 cm. Columns of this length allowed the uranium extraction to be completed before the pink peroxy-vanadium band reached the bottom of the column. The formation of peroxy-vanadium compounds was later avoided by the use of fresh peroxide-free ether.

RECOMMENDED METHOD FOR SILICEOUS ORES

REAGENTS—

Cellulose pulp—This should be prepared as described on p. 397.

Ether - nitric acid solvent—A 5 per cent. v/v solution of nitric acid in ether prepared by mixing 5 ml of nitric acid, sp.gr. 1·42, with 100 ml of dry peroxide-free ethyl ether.

Nitric acid—Concentrated, sp.gr. 1·42.

PROCEDURE—

Weigh about 2·5 g of sample into a platinum dish. Add 2 ml of concentrated nitric acid, sp.gr. 1·42, and 5 ml of hydrofluoric acid and evaporate the mixture just to dryness on a hot-plate. Wash the sample with a minimum of water into a 100-ml beaker. After evaporation to dryness, add 10 ml of concentrated nitric acid and again evaporate the solution just to dryness. Redissolve the residue in 8 ml of water containing 2 ml of concentrated nitric acid.

Prepare a cellulose column, as described on p. 397, 7·5 cm in length, and wash it through with 100 ml of ether - nitric acid solvent. Adjust the solvent level in the column until it coincides with the top of the cellulose.

Add sufficient cellulose pulp to the solution of the sample to absorb completely the aqueous nitric acid solution. Stir the mixture thoroughly with a glass rod. Transfer the wad containing the absorbed sample to the top of the extraction column with the aid of the glass rod. Wash final traces into the column with not more than 10 ml of ether - nitric acid solvent from a wash bottle; care must be taken to avoid "ether creep." Break up the pulp containing the sample with a glass plunger and gently press it down to form a continuation of the original column of cellulose. Remove the clip and tubing from the bottom of the column and allow the ether to run out into a 250-ml Kjeldahl flask until the level of ether solution in the extraction tube reaches the top of the cellulose column. Add a further 10 ml of ether - nitric acid solvent to the top of the extraction tube and repeat the procedure with successive 10-ml portions of the solvent mixture until 100 ml of eluent have been collected. Use each 10 ml of ether - nitric acid mixture to wash out the sample beaker.

Add 50 ml of water to the eluent ether solution and remove the organic solvent by distillation on a steam-bath. Add 5 ml of sulphuric acid and 5 ml of perchloric acid to the aqueous solution and evaporate to fuming. Complete the estimation by any suitable method.[3,4]

RESULTS—

It was not found necessary to increase the volume of ether required for extraction beyond 100 ml when using a 7·5-cm column. Results obtained on columns of this length with 2·5-g portions of ore are shown in Table X. It was considered that these results demonstrated the suitability of the method for the analysis of low-grade siliceous materials.

TABLE X

EXTRACTION OF URANIUM FROM SILICEOUS ORES BY RECOMMENDED METHOD

Sample	Molybdenum added, mg	Vanadium added, mg	U_3O_8 by cellulose column, %	U_3O_8 by standard chemical methods[3,4] (mean value), %
11	nil	25	2·14	2·13
11	25	nil	2·17	2·13
14	25	25	0·06	0·06
13	25	25	0·57	0·54
13	nil	nil	0·55	0·54
13	25	25	0·54	0·54
15	25	25	2·09	2·16
16	25	25	2·88	2·89
17	25	25	3·35	3·16

APPLICATION TO ANALYSIS OF MONAZITE SANDS AND OTHER REFRACTORY ORES

The application of the cellulose column technique to the analysis of monazite sands presented several difficulties. A fusion was necessary in order to obtain a nitrate solution of the mineral, and this gave rise to the presence of large amounts of neutral salts in the test solution. Most of the ores contained considerable quantities of phosphate, which inhibited the extraction of uranium; others contained large amounts of zirconium, which was partly extracted. The addition of ferric nitrate to the test solution overcame the retaining effect of phosphate and addition of tartaric acid prevented the extraction of zirconium. A large amount of cellulose was needed to absorb the test solution, the volume of which was increased to cater for the high concentration of potassium salts, but this large wad did not impair the extraction of uranium. A number of different types of mineral have been studied, including "pure monazites," consisting mainly of rare earth and thorium phosphates; "crude monazite," consisting of a small quantity of monazite with a large quantity of other refractory ores; and zircons, which were mainly zirconium silicate. The development of the method is described immediately below.

SOLUTION OF THE SAMPLE—

In order to obtain a nitric acid solution of monazite, advantage was taken of the observation that treatment of the sample with hydrofluoric acid followed by fusion with potassium hydroxide gave a melt that was soluble in nitric acid. This procedure was improved by fusing with potassium hydroxide, dissolving in nitric acid and then adding dilute hydrofluoric acid to the solution. Except for a trace of gelatinous silica, complete solution was obtained. Excess hydrofluoric acid was avoided, as it precipitated thorium and the rare-earth fluorides. With a pure monazite, 2 or 3 drops of a 2 per cent. solution of hydrofluoric acid were found sufficient. The same effect was obtained by the addition of potassium bifluoride to the potassium hydroxide fusion, but addition of hydrofluoric acid, as described, was preferred, because potassium bifluoride rapidly attacked the nickel crucible. The amount of potassium hydroxide required for fusion varied with each sample, but for pure monazite a 5 to 1 ratio of potassium hydroxide to sample, heated for 30 minutes at red heat, was found sufficient to ensure complete breakdown, although for crude monazite the ratio was increased to 8 to 1 and the heating time to 1 hour. For the present work, 2·5-g portions of sample were used for each estimation.

EXTRACTION OF URANIUM—

Initial experiments with a 25-cm column of cellulose showed that uranium could be completely extracted by 300 ml of ether containing 5 per cent. v/v of nitric acid. The nitric acid solution of the sample was evaporated to about 25 ml, 4 ml of water were added and the resultant solution was absorbed on a wad of cellulose. During these experiments it was noticed that a dark orange band, identified as cerium in the ceric state, moved rapidly down the column and coloured the effluent. This did not affect the result if a titrimetric finish was used, but interfered with a colorimetric determination. Since cerous nitrate showed little movement in the column, further experiments were made with a ferrous sulphate trap to reduce cerium. This method was found to hold back cerium satisfactorily and results are shown in Table XI for extractions both with and without the ferrous sulphate trap.

TABLE XI

EXTRACTION OF URANIUM FROM PURE MONAZITE SANDS USING A 25-CM COLUMN

Sample	Volume of ether, ml	U_3O_8 found, %	U_3O_8 found (mean value), %	U_3O_8 by standard chemical methods[3,4] (mean value), %
Without ferrous sulphate trap—				
1	500	0·41	0·37	0·37
1	300	0·33		
1	300	0·37		
1	300	0·35		
1	300	0·40		
With ferrous sulphate trap—				
2	300	0·36	0·38	0·37(5)
2	300	0·37		
2	300	0·40		
2	300	0·39		
2	300	0·38		
1	300	0·37	0·37	0·37
1	300	0·37		
3	300	0·35	0·35	0·37
4	300	0·41	0·41	0·36

As about 8 g of cellulose were used in absorbing the solution of the sample, the total length of both wad and column, when a 20-cm column was used, was about 50 cm. In an attempt to use a column of more manageable length, experiments were carried out with a 5-cm column of cellulose. Addition of hydrogen peroxide to reduce cerium was also tried, as being a more convenient method than the use of a ferrous sulphate trap. About 2 ml of 20-volume hydrogen peroxide were added to the nitric acid solution of the sample while it was being evaporated to dryness. Figures shown in Table XII indicate that satisfactory extraction of uranium is obtained with a 5-cm column and 100 ml of ether - nitric acid solution.

TABLE XII

EXTRACTION OF URANIUM FROM PURE MONAZITE SANDS WITH A 5-CM COLUMN

Sample	Length of column, cm	Volume of ether, ml	U_3O_8 found, %	U_3O_8 found (mean value), %	U_3O_8 by standard chemical methods[3,4] (mean value), %
1	25	300	0·37	0·37	0·37
1	25	300	0·37		
1	5	300	0·37		
1	5	100	0·37		
1	5	100	0·37		
5	5	100	0·39	0·39	0·36
6	5	100	0·34	0·34	0·30

EFFECT OF ZIRCONIUM AND PHOSPHORIC ACID ON THE EXTRACTION PROCESS—

The materials so far studied were all pure monazite samples. When the method was applied to crude monazites, particularly those containing a large amount of zircon, difficulty was encountered from some zirconium passing through the column and contaminating the eluent. The results of uranium determinations on samples containing zirconium were very erratic, as shown in Table XIII.

TABLE XIII

THE EFFECT OF ZIRCONIUM ON THE EXTRACTION OF URANIUM FROM CRUDE MONAZITES

Sample	Length of column, cm	Volume of ether, ml	U_3O_8 found, %	U_3O_8 by standard chemical methods[3,4] (mean value), %
7	25	300	0·54	0·48
8	25	300	0·06	0·05
9	25	300	0·32	0·25
10	25	300	0·18	0·18
7	5	100	0·42	0·48
7	5	100	0·46	0·48
7	5	100	0·35	0·48
8	5	100	0·07	0·05
10	5	100	0·26	0·18
10	5	100	0·21	0·18

Accordingly, factors affecting the movement of zirconium were investigated in the following manner. A known weight of zirconium nitrate was dissolved in 10-ml portions of nitric acid of various strengths. Each 10 ml of solution was taken up on a wad of cellulose and extracted in a 5-cm column with 100 ml of ether containing 5 per cent. v/v of nitric acid. The movement of zirconium down the column was measured and showed (see Table XIV) an increase with increasing nitric acid concentration. If, however, a nitric acid solution of crude monazite was evaporated to complete dryness, redissolved in 5 or 10 per cent. v/v nitric acid and extracted in a 5-cm column, zirconium was still found in the ether eluent. The increased movement of zirconium under these conditions was not due to a salting out effect of potassium nitrate, as shown in the last line of Table XIV, but in other experiments, ferric nitrate has been shown to produce such an effect.

Although zirconium was still extracted from crude monazite dissolved in a 10 per cent. v/v solution of nitric acid after fusion with potassium hydroxide, the amount extracted was very much smaller than if a stronger solution of nitric acid was used. In all further estimations, therefore, the acidity was controlled by evaporating the nitric acid solution of the sample to dryness and redissolving in 20 ml of 10 per cent. v/v nitric acid. As a

TABLE XIV

BEHAVIOUR OF ZIRCONIUM WITH VARIATION OF ACID CONCENTRATION

Weight of zirconium nitrate taken = 0·1 g

Volume of nitric acid solution, ml	Strength of nitric acid solution, % v/v	Movement of zirconium down column, cm	Added potassium nitrate
10	10	2·5	nil
10	15	2·5	nil
10	20	3·0	nil
10	25	4·5	nil
10	30	>5·0	nil
8	25	5·0	nil
20	10	3·0	20 g

small amount of zirconium still passed through the column, investigations were made into means of preventing the movement by complex formation. Addition of phosphoric acid to the nitric acid solution of the sample held back zirconium but slowed down the extraction of uranium. Traps of ferrous sulphate, oxalic acid or activated carbon in the column were not successful; extraction with ether containing 5 per cent. v/v of nitric acid and 1 per cent. v/v of orthophosphoric acid still resulted in zirconium being found in the eluent. Addition of sulphuric acid to the nitric acid solution of the sample did, however, result in complete retention of zirconium and so permitted extraction of uranium. In this procedure the nitric acid solution of the sample was evaporated to dryness, redissolved in 20 ml of 10 per cent. v/v nitric acid. Sulphuric acid, 6 ml of a 1 + 1 solution, was added and the mixture was boiled for 2 or 3 minutes. Zirconium was completely held back on extraction in a cellulose absorption column. The results for a series of crude monazite samples treated with sulphuric acid in the above manner are shown in Table XV.

TABLE XV

ADDITION OF SULPHURIC ACID AS COMPLEXING AGENT FOR ZIRCONIUM

Sample	Type	U_3O_8 found, %	U_3O_8 by standard chemical methods[3,4] (mean value), %
11	Zircon concentrate	0·045	0·05
11	„	0·041	
8	Crude monazite	0·048	0·048
8	„	0·047	
8	„	0·051	
8	„	0·051	
8	„	0·048	
10	„	0·16	0·18

The amount of sulphuric acid added is large, but this quantity was found necessary to cope with samples 10 and 11, which had a high zircon content. The efficiency of extraction under these conditions was shown by addition of a weighed amount of U_3O_8 to a sample of known uranium content and finding the amount of added uranium extracted, as follows—

Sample No. 8: Weight of U_3O_8 added = 25 mg.
Weight of U_3O_8 recovered = 24·8 mg.

The results shown in Table XV were found for ores with a low monazite content. When the method was applied to pure monazite, the extraction of uranium was very poor. This was owing to retention of uranium brought about by the large excess of uncomplexed sulphate present in the absence of a high concentration of zirconium.

USE OF TARTARIC ACID AND FERRIC NITRATE AS COMPLEXING AGENTS FOR ZIRCONIUM AND PHOSPHORIC ACID—

Addition of either oxalic or tartaric acids to the nitric acid solution of a sample of monazite before absorption on a wad was found to complex zirconium satisfactorily. The procedure used was to evaporate the nitric acid solution of monazite to dryness, redissolve in 20 ml of 10 per cent. v/v nitric acid, add 2 ml of 20-volume hydrogen peroxide, boil for a few minutes, add 3 g of the organic acid and then cool. The use of either acid resulted in a lower rate of extraction of uranium, particularly with pure monazite, but whereas a 50 per cent. increase in the volume of ether - nitric acid solution used in extraction resulted in complete recovery of uranium when tartaric acid was used, results were still low for oxalic acid. Of the two organic acids, oxalic is the more effective complexing agent for zirconium, but tartaric acid retains zirconium sufficiently well to enable a clean extraction of uranium to be achieved. Increasing the concentration of the nitric acid in the solution of the sample before extraction did not materially affect the extraction of uranium, although some increase in the movement of zirconium was apparent.

During these estimations it was noticed that, if an iron crucible was used for the fusion, results were satisfactory, but if a nickel vessel was used, the values were low. Experiments were then carried out in which fusion was carried out in a nickel crucible, but iron as ferric nitrate was added to the nitric acid solution of the sample before extraction. Under these conditions uranium was quantitatively extracted. Since a clean, easily removed melt was obtained in nickel crucibles, they were preferred and ferric nitrate was added at a later stage of the estimation.

TABLE XVI

USE OF TARTARIC ACID AS A COMPLEXING AGENT FOR ZIRCONIUM

Sample	Type	Volume of ether, ml	Strength of nitric acid used for solution of sample, % v/v	Weight of ferric nitrate added, g	U_3O_8 found, %	U_3O_8 present, %
With added tartaric acid—						
10	Crude	100	10	nil	0·18	0·18
10	"	100	10	nil	0·20	0·18
1	Pure	100	10	nil	0·24	0·37
1	"	100	10	nil	0·27	0·37
1	"	100	25	nil	0·27	0·37
1	"	150	25	nil	0·33	0·37
1	"	100	10	5	0·32	0·37
1	"	150	25	5	0·37	0·37
With added oxalic acid—						
10	Crude	100	10	nil	0·13	0·18
10	"	150	10	5	0·19	0·18
1	Pure	100	10	5	0·32	0·37
1	"	150	25	5	0·33	0·37
1	"	150	25	5	0·34	0·37

As a result of these experiments, summarised in Table XVI, the addition of tartaric acid and ferric nitrate was included in the procedure recommended for the analysis of uranium in monazite sand.

RECOMMENDED METHOD FOR MONAZITE SAND AND REFRACTORY ORES

REAGENTS—

Cellulose pulp—This should be prepared as described on p. 397.
Ether - nitric acid solvent—A 5 per cent. v/v solution prepared as described on p. 402.
Potassium hydroxide—Solid.
Nitric acid—Concentrated, sp.gr. 1·42.
Hydrofluoric acid—A 2 per cent. v/v aqueous solution.

PROCEDURE—

Heat 12·5 to 20 g of potassium hydroxide, according to the type of mineral to be analysed, in a nickel crucible until all the water has been removed. Allow to cool slightly, add 2·5 g of sample and quickly cover the crucible with its lid. Heat the melt slowly to red heat. Continue to heat for 1 hour at bright red heat, occasionally swirling the contents of the crucible. Allow the crucible to cool and wash the contents with water into a 400-ml beaker. Make just acid with nitric acid and then add about 20 ml of concentrated acid in excess. Bring the solution to the boil with constant stirring and slowly add dropwise a 2 per cent. solution of hydrofluoric acid. Stop the addition of hydrofluoric acid as soon as the solution clears and evaporate to dryness on a steam-bath or under an infra-red lamp. To the residue add 20 ml of water containing 2 ml of concentrated nitric acid and 5 g of ferric nitrate. Heat with stirring until solution is complete. Add 2 ml of 20-volume hydrogen peroxide and boil for 2 or 3 minutes to reduce cerium. Then add 3 g of tartaric acid, stir and cool rapidly.

To the nearly solid mass add about 8 g of cellulose pulp and stir until a homogeneous mixture is attained. Pack an extraction tube to a depth of 5 cm with cellulose and wash the column by allowing 100 ml of ether - nitric acid solvent to flow through it. Adjust the ether level until it is about 10 cm above the top of the column. Transfer the wad containing the sample in small portions to the extraction tube. Break up each portion of pulp with a glass plunger and gently press down to form a continuous column with the original cellulose.

Remove the clip and tubing from the bottom of the extraction tube and allow the ether to run out into a 350-ml Kjeldahl flask until the level of the ether - nitric acid solution in the extraction tube reaches the top of the cellulose column. Add a further 10 ml of ether - nitric acid solution to the top of the extraction tube and repeat the procedure with successive 10-ml portions of the solvent mixture until 150 ml of eluent have been collected. Use each 10-ml portion of ethereal solvent to wash out the sample beaker. Add 75 ml of water to the eluent ether solution and remove the organic solvent by distillation on a steam-bath. Add 5 ml of sulphuric acid and 5 ml of perchloric acid to the aqueous solution and take the mixture to fuming. Complete the estimation by any suitable method.[3,4]

RESULTS—

Satisfactory results, as shown in Table XVII, were obtained on both pure and crude monazite minerals.

TABLE XVII

EXTRACTION OF URANIUM FROM MONAZITE SANDS BY THE RECOMMENDED METHOD

Sample	Type	U_3O_8 found, %	Mean U_3O_8 by standard chemical methods[3,4]
1	Pure	0·37, 0·36	0·37
7	Crude	0·50	0·48
8	,,	0·05	0·05
10	,,	0·19	0·18
12	Pure	0·35, 0·35	0·35
13	Crude	0·09, 0·07	0·07
14	Pure	0·38, 0·42, 0·39	No reliable results obtained by other methods
15	,,	0·86, 0·81, 0·85	
16	,,	0·92, 0·96	
17	,,	0·26, 0·28, 0·30	
18	Crude	0·35, 0·33, 0·33	

The efficiency of the extraction, as shown in Table XVIII, was tested by addition of uranium to a standard sample of monazite of known uranium content. A determination of the total uranium was made and the "recovery" calculated by subtracting the known uranium content of the sample.

TABLE XVIII

RECOVERY OF URANIUM ADDED TO MONAZITE SAND

Sample No. 1	
Weight of U_3O_8 added, mg	Weight of U_3O_8 recovered, mg
5·0	4·96
10·0	10·07
25·0	24·94

The agreement between the two methods shown in Table XVII and the recoveries shown in Table XVIII are considered satisfactory. In spite of the special precautions necessary to prevent the movement of zirconium, the cellulose column method is preferred to normal chemical methods because of its ease and speed of operation and the accuracy and reproducibility of the results.

The authors wish to thank J. G. Beynon, Miss R. D. Humphreys, Mrs. P. J. Forrest and Miss P. McGlone for assistance in the experimental work.

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DISCUSSION

MR. C. G. DAUBNEY enquired about the time taken for ether to run through a column, the prevention of evaporation during the percolations, and any precautions that must be taken to avoid an increase in the amount of water present.

MR. BURSTALL replied that a normally packed column permitted a flow-rate of 100 ml of ethereal solvent in 20 to 30 minutes. The eluent was collected directly in a distillation flask and no special precautions were taken to prevent evaporation or to prevent an increase in the water content of the solvent. Addition of more water to the solvent tended to slow up the extraction of uranium slightly, but at the same time the movement of other materials also was usually retarded.

DR. G. E. FOSTER asked whether the presence of peroxide in the ether would affect the results.

MR. BURSTALL said that peroxide in the ether should be avoided. A peroxy-vanadium compound readily soluble in the solvent was formed if vanadium was present. This substance moved down the column as a characteristic pink zone immediately following the uranium.

MR. W. H. BENNETT asked, first, whether fluorides could be tolerated in the separations as described and secondly, whether the authors would comment on the use of water-repellent agents other than the toxic compound quoted in the paper.

MR. WELLS said, in reply, that the presence of fluoride should be avoided because free hydrofluoric acid would remove the silicone lining from the glass tube. Hydrofluoric acid, unless suitably complexed, would also inhibit the extraction of uranium. Another, less toxic, silicone solution was now available; it was manufactured by the Dow Corning Co. of America, and marketed in this country by Albright & Wilson under the name "Dow Corning Fluid 200."

DR. D. I. COOMBER asked whether the authors had had any experience of the use of derivatives of cellulose, for example, ethyl cellulose, in this or related problems. He thought that, with substituted celluloses, metals other than uranium would probably not be held back so much. If carboxymethyl cellulose were used the column would become an ion-exchange column rather than a chromatographic column.

MR. BURSTALL said that ethyl cellulose had not, so far, been examined as an adsorbent.

MR. N. STRAFFORD asked whether the authors considered the separation by cellulose to be due to partition or to adsorption chromatography. Had they tried partition chromatography on wet silica gel?

MR. BURSTALL replied that the separations possible on cellulose appeared to be due to a combination of both partition and adsorption, the predominance of either factor depending upon the metal and solvent concerned. Partition chromatography on wet silica gel has been tried for a number of inorganic separations, but without much success.

DR. J. H. HAMENCE asked the authors if they would put forward any theories that they might have arrived at in the course of their work on the mechanism of the separation. In view of the ever-increasing application of chromatography in the solution of hitherto insoluble problems, information on the mechanism of the phenomenon was always very valuable, particularly as a guide when working out conditions for a new separation. In the questioner's experience, adsorption and solubility appeared to play the major parts in this work.

MR. WELLS replied that a number of factors combined to effect a separation. The extent to which any one of these factors contributed to a separation varied considerably and difficulty was frequently experienced in obtaining precise information as to which factor predominated.

The solubility of the material in the solvent used was an obvious first consideration. Generally, the next most important factor is the extent of partition of the material between solvent and water in the cellulose. Finally, the retention of a number of metallic salts by cellulose appeared to be far too strong to be accounted for by partition alone and for these it was possible that chemi-adsorption occurred.

DR. W. STROSS asked whether the authors had found applications of this extremely elegant selective technique (perhaps with suitable modifications) to the determinations of elements other than uranium.

MR. BURSTALL said that a similar chromatographic technique had been used in a number of other separations and determinations, some of which had been published and others were to be published in the near future. These studies included the separation and estimation of nickel, cobalt, copper and iron in samples of nickel steel, the separation and determination of gold in the platinum metals, of mercury with the group IIA metals, thorium in minerals and ores, niobium and tantalum in minerals and ores and the separation of zirconium and hafnium.

DR. H. LIEBMANN referred to Dr. Stross's question and mentioned that, following very closely the methods of Burstall and his colleagues and using the polarograph for the final analysis, they had recently determined small quantities of zinc in tin - lead solders. At present they could estimate quantities of about 0·001 per cent. in a 2-g sample, but they believed that the sensitivity of the method was capable of improvement. It was hoped to publish a preliminary Note on this subject in the near future.

MR. R. C. CHIRNSIDE said he would be glad to know if the work that the authors had so far carried out enabled them to give a lead as to the probable behaviour of some of the non-metals, particularly boron and arsenic, on these chromatographic columns.

MR. BURSTALL replied that, although they had not studied the extraction of boron or arsenic by chromatographic means, separations that had been carried out on strips of filter-paper by the authors and others indicated that it should be possible to develop an extraction procedure for these materials.

The Rapid Determination of Sodium and Potassium in Rocks and Minerals by Flame Photometry

BY G. H. OSBORN AND H. JOHNS

(Presented at the meeting of the Physical Methods Group on Friday, October 6th, 1950)

A method is outlined for the rapid and accurate determination of sodium and potassium in rocks and minerals by means of the flame photometer. It is shown that the method gives results that compare favourably with those obtained elsewhere by classical procedures, and that the saving in time required for an analysis is very great. It is also shown that the sodium and potassium may be determined, if necessary, when only very small amounts of material are available.

THE usual method for the chemical analysis of sodium and potassium in rocks and minerals is that of Lawrence Smith,[1] which consists essentially in fusing an intimate mixture of one part of ground rock with one part of ammonium chloride and eight parts of calcium carbonate, extracting in water and filtering to remove the silicates and aluminates of calcium, and the carbonates of iron, calcium and magnesium. The alkalis pass into the filtrate as chlorides. The rest of the procedure consists in the precipitation of the excess of lime by means of ammonium carbonate, expulsion of ammonium salts by heating the evaporated filtrate, removal of the last traces of lime, conversion of the traces of alkali sulphates to chlorides, weighing the mixed alkali chlorides and, finally, the separation and weighing of the potassium either as the perchlorate or chloroplatinate, with the estimation of sodium by difference.

The drawbacks to this method are: (*a*) the time required by even an experienced operator is excessive—Haslam and Beeley,[2] in a critical review of the method, state that they found it difficult to complete the sodium and potassium determinations in less than three days; (*b*) great manipulative skill is required; (*c*) a blank determination must be made for all the reagents; (*d*) there is great risk of loss of the alkalis by occlusion when filtering from the insoluble silicates, aluminates and carbonates, so that several reprecipitations are required for highly accurate work; (*e*) there is risk of loss of alkalis at the final volatilisation of ammonium salts. Despite its limitations this method is still very widely used in mineral analysis, as other chemical methods have not been shown to possess any outstanding advantages. Haslam and Beeley[2] also proposed a modification of the method for which they claimed increased accuracy, but stated that whilst the sodium determination could normally be completed in one day, the following day was required to complete the potassium determination. In this modification sodium is determined as the zinc uranyl acetate complex and the potassium, if present in small amounts, as the cobaltinitrite or, if in large amounts, as the perchlorate.

Various authors, including Mitchell[3] and Muller,[4] in an attempt to simplify and speed up the determination, have proposed spectrographic methods. Lundegardh and Mitchell in early experiments introduced a suitable solution of the mineral into an air - acetylene burner by means of an atomiser, passed the emitted light through a spectrometer and photographed the spectrum; the density of the spectral lines was measured by means of a photometer and compared with a composite standard solution analysed in the same manner. The results were promising, but the technique was intricate and time-consuming.

Mitchell and Robertson[5] noted that the intensity of the light emitted by an ion was not a simple function of its concentration in solution, but varied in a complicated manner depending on the presence or absence of certain other ions in solution. With the Lundegardh apparatus these authors observed that calcium and strontium flames were strongly depressed by aluminium, but that in the presence of an excess of calcium the depression of strontium by aluminium was considerably diminished. In controlled conditions this depression could be made use of for the indirect determination of aluminium.

Many other similar interferences have been observed, both with anions and with cations, *e.g.*, the emission from alkali metals is reduced slightly by sulphates and tartrates and very much by phosphates. More recent developments of spectrophotometric analysis have been largely concerned with studies of these and other interferences and with attempts to reduce them.

The direct reading photo-electric photometer made it possible to carry out analysis much more rapidly, with consequent reduction in the errors caused by fluctuations in gas and air pressure. In some of these instruments a desired waveband is scanned through selective filters, but the difficulty of obtaining spectrally pure filters makes the more versatile instruments that are provided with monochromators much to be preferred.

Two different methods have been used for relating intensity of light to concentration of the ion in solution.

In the absolute method a calibration curve is drawn for solutions of known concentrations, gas, air and oxygen pressures being kept constant within fine limits. The concentrations of unknown solutions can then be determined by interpolation on the graph. The objection to this method is that interference from foreign ions may affect the sample, but not the calibrating solution, and that these interferences may be entirely unsuspected. Attempts have been made to obviate these effects by preparing calibration solutions that imitate as closely as possible the composition of the sample to be examined. For the determination of alkali metals in cement, a method has been described[6] in which a blank solution of calcium oxide in hydrochloric acid is used as a base for the calibration solution. Excellent results are claimed, and it is possible that this method is satisfactory for simple routine analysis, but for more complex materials, such as rocks and minerals, containing an unknown and probably large number of constituents in unknown concentration, such an artifice would be impracticable.

A recent paper[7] described the addition of "radiation buffers" to calibration solutions and to samples under test. The addition consists of a large excess of an interfering ion, so that further effects due to trace constituents in the sample are negligible.

A serious objection, however, to all calibration methods is that light intensity depends on many variable factors that cannot always be reproduced after an interval of time. Possibly the most difficult factor to control is rate of atomisation, which depends on air pressure, the viscosity and temperature of the solution and the width of the orifice. Slight clogging of the orifice changes the flame response profoundly.

The internal-standard method, inherited from arc spectrography, has been claimed to be less affected by interferences.[8] A known small amount of a foreign ion is deliberately added to the material to be examined and the light intensity due to this ion is then compared with the light intensity due to the ion sought. A dual optical system is used so that fluctuations in pressure, viscosity and temperature are avoided. The internal standard is normally chosen so that its properties resemble those of the element sought, *e.g.*, lithium is used in determination of sodium and potassium. Interfering effects are, however, not necessarily the same for two different ions, even if they are closely related, and in examining unknown solutions a further uncertainty is introduced by the internal-standard method, as the material may already contain some of the reference element.[6] For these reasons it is difficult to apply the internal-standard method with precision to the analysis of rocks, although it is certainly satisfactory for such determinations as the sodium and potassium content of blood serum.

With the shortcomings of the two methods in general use in mind, the possibility was considered of determining alkali metals by a direct addition method, *i.e.*, by measuring the response of the sample and then measuring the increase in light intensity on adding a small amount of standard alkali to a suitable aliquot. It was thought that, by taking readings for several aliquots containing different quantities of standard, a graph could be constructed and extrapolated to determine the amount of alkali present in the sample. The usual interference effects should in this manner be entirely obviated.

Extrapolation is satisfactory only if the graph is perfectly regular and preferably linear. Experimental work demonstrated that potassium gave an almost linear graph at low concentrations (0 to 10 p.p.m.) but that sodium gave a slightly curved graph even at this very small concentration. Calcium gave a linear response up to 500 p.p.m.

Mr. B. S. Cooper has suggested that the parabolic shape of these graphs is due to absorption of light from the rear part of the flame by the vapour of the substance in the front of the flame. It is possible that a more linear response would result from the use of a relatively flat flame of the "fish-tail" type, and experiments are being conducted to investigate this point.

Alternatively, saturation emission may be prevented by working at very low concentrations or by the addition of foreign ions known to depress emission. It has already been mentioned that certain anions depress the amount of light emitted by alkali metals, and that the phosphate ion in particular causes a large depression. The effect of phosphate ions on the shape of the graph of sodium concentration *versus* light intensity was therefore investigated. The results showed that for concentrations up to 20 p.p.m. the graph was perfectly linear, and very much less steep than in the absence of phosphate. Similar results were obtained for potassium.

The reduction of light emission in the presence of foreign substances may be due to restricted ionisation, leading to a molecular, rather than an ionic spectrum, but other factors such as absorption and alteration of flame temperature may play a part. Nitrogenous organic substances may, for instance, be expected to lower the flame temperature if they are present in a large excess, and a similar effect is possible in the presence of halogenated paraffins. However, in a series of experiments, no reduction in light intensity was observed on addition of pyridine or chloroform to a sodium solution, although a small decrease was brought about by addition of an excess of urea. Other organic substances such as acids and phenols were also found to have little or no effect, and it was concluded that at the temperature of the flame organic molecules are, for the most part, completely destroyed. It has been reported[9] that light emission is actually increased by the addition of alcohol and acetic acid, and these results have been verified by experiment. It is probable that this is a physical effect resulting from an increased rate of atomisation owing to the lowered surface tension of the test solution.

Inorganic ions that were found to suppress emission of light from sodium include phosphate, borate and molybdate, which are all about equally effective, and may in some circumstances reduce the light intensity by more than half. A smaller effect is produced by addition of an excess of sulphate, but nitrate, chromate and halides give the same response as the free base.

The effect of some of these anions is shown in Figs. 1 and 2, which were prepared by plotting readings on the Beckman photometer against concentration of sodium or potassium in parts per million.

The curves did not pass through the origin as the galvanometer is slightly deflected even when no sodium is intentionally vaporised in the flame. This effect is due to flame background and to traces of sodium in the air and the water used for preparing solutions, and is measured by vaporising pure distilled water into the flame.

In order to investigate the effect of cations, series of readings were taken to compare pure dilute solutions of sodium and potassium salts with solutions of various salts containing the same quantity of added alkali. In the first series the equivalent of 20 parts per million of sodium, as chloride, was added to various 1 per cent. solutions of metal chlorides. It was observed that the intensity of light at 5893 A was reduced by about 20 per cent. by ammonium, cupric, zinc, cadmium, magnesium, ferric, cobalt and nickel chlorides, with no appreciable difference in effect between any of these ions. Smaller effects were observed with barium and calcium chlorides, the depression being about 15 per cent. In the presence of lithium and potassium chlorides no decrease in intensity of sodium emission was detected.

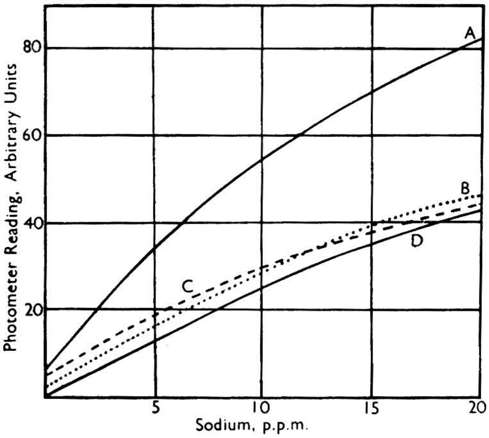

Fig. 1. Effect of anions on sodium

Curve A, free base; curve B, solution in 1 per cent. boric acid; curve C, solution in 1 per cent. ammonium molybdate; curve D, solution in 1 per cent. ammonium phosphate

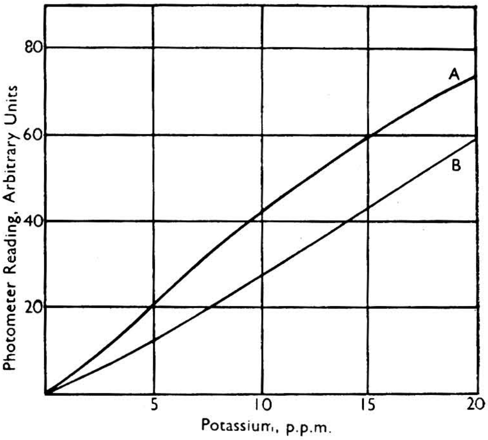

Fig. 2. Effect of anions on potassium

Curve A, free base; curve B, solution in 1 per cent. ammonium phosphate

In a second series, sodium as nitrate was determined in other nitrate solutions. Approximately uniform depression of about 20 per cent. was noted when the sodium was determined in 1 per cent. solutions of silver, aluminium, lead, cerium, lanthanum and uranium as nitrates.

Similar results were obtained on repeating these investigations with potassium instead of sodium. It appears from these preliminary results that any solids, other than alkalis and alkaline earths, have the effect of depressing the intensity.

These findings were applied to the analysis of rocks and minerals by finely grinding a number of samples and analysing them on the Beckman flame spectrophotometer, model DU.

PROCEDURE

Use wavelengths of 5893 A for sodium and 7670 A for potassium; these are the principal lines for these elements.

With a slit width of 0·1 mm, pass propane into the burner until a pressure of 2 cm is registered on the manometer. Then start the oxygen supply and increase it until a non-luminous flame is produced. Operate the atomiser at a pressure of 25 lb. At the wavelengths specified the flame background will be found to be very slight.

Weigh 0·1 g of finely ground material in a platinum dish and moisten it with 1 drop of sulphuric acid. Evaporate to dryness with 2 ml of hydrofluoric acid. If decomposition is not complete, repeat the evaporation with hydrofluoric acid. Dissolve the residue by boiling it with 10 ml of 5 N hydrochloric acid. Dilute the solutions to 500 ml with a 1 per cent. solution of ammonium phosphate. Then take four 100-ml aliquots and add to them 0, 0·1, 0·2 or 0·3 ml respectively of 0·1 N alkali according to the elements being determined. The ammonium phosphate must previously have been examined for sodium and potassium on the flame photometer. Normally, the amount present should not exceed 0·1 p.p.m. in a 1 per cent. solution.

MEASUREMENT—

When different solutions are vaporised, the flame intensity is measured in arbitrary units as follows—

(*a*) Prepare a reagent blank by evaporating hydrofluoric and sulphuric acids in the quantity used for the decomposition of the rock specimen and treat as described above.

(*b*) Use a prepared solution of the sample under examination.

(*c*, *d* and *e*) Use solution (*b*) containing 0·1, 0·2 and 0·3 ml respectively of 0·10 N sodium hydroxide in 100 ml.

If the increase in flame intensity between (*c*), (*d*) and (*e*) does not indicate a rectilinear relationship between concentration and light emitted, all the solutions are diluted with water and the determinations repeated. When the dilution has been so adjusted that a constant difference is found between (*c*), (*d*) and (*e*), the percentage of Na_2O equals—

$$\left(\frac{b - a}{c - b}\right) \times 31/10^5 \text{ percentage of solution.}$$

Owing to the limited linearity of the curve, greater accuracy is obtained if the value of (*b*) is kept fairly small in the above equation. If a very large deflection is obtained it is advisable to dilute the sample solution 10- or 100-fold and to repeat the determination.

Some results by the above technique are shown in Table I and compared with results for the same specimens found by Dr. Max Hey of the British Museum of Natural History by the classical Lawrence Smith method of weighing the mixed chlorides of sodium and potassium, determining potassium as the perchlorate and calculating Na_2O by difference.

TABLE I

COMPARISON OF RESULTS BY SPECTROPHOTOMETRIC AND CHEMICAL METHODS FOR SODIUM

Sample		Na_2O by chemical analysis, %	Na_2O by flame spectrophotometer, %	Difference, %
1516	Rhyolite, Lupata Gorge, Nyasaland ..	1·97	2·16	+0·19
2358	Black manganese ore (46% of MnO), Benallt, N. Wales	0·27	0·31	+0·04
2253	Limestone, Nyasaland	0·03	0·15	+0·12
2194	Quartz - alkali - syenite, Lion Rock Gully, Nyasaland	3·88	4·09	+0·21
2361	Chloritic mudstone, country rock of manganese ores, Benallt, N. Wales ..	0·14	0·20	+0·06
2193	Felspar - pyroxene rock, Nkalonge Hill, Nyasaland	0·27	0·36	+0·09
2018	Phenolite dike, Maize Hill, Nyasaland	10·73	11·00	+0·27
2359	Grey phosphatic manganese ore (17% of MnO, 10% of P_2O_5), Benallt, N. Wales	nil	0·07	+0·07
2067	Basalt, Teliki Volcano, Kenya	4·14	4·13	−0·01
1907	Biotite-bearing algerine - augite foyaite, Nyasaland	8·25	8·36	+0·11

The results with the flame spectrophotometer are usually slightly higher than those by chemical methods, but this is satisfactory if the probable loss by occlusion or volatilisation in the gravimetric method is accepted. When no sodium was detected gravimetrically we are convinced it was present in small amounts. Moreover, the concordance is much better than that of the figures quoted by Hillebrand and Lundell[10] for sodium determinations on the same rock made gravimetrically by different analysts.

The corresponding figures for potassium are shown in Table II.

TABLE II

COMPARISON OF RESULTS BY SPECTROPHOTOMETRIC AND CHEMICAL METHODS FOR POTASSIUM

Sample	K_2O by chemical analysis, %	K_2O by flame spectrophotometer, %	Difference, %
1516	4·86	4·86	nil
2358	nil	0·11	+0·11
2194	6·28	6·23	−0·05
2361	0·48	0·59	+0·11
2193	14·68	14·70	+0·02
2018	4·72	4·53	−0·19
2359	nil	0·04	+0·04
2067	1·91	1·90	−0·01
1907	7·53	7·64	+0·11

It will be observed that the agreement is even better than that for sodium, and that although the deviation is random in direction, it is, as before, mostly in the positive direction, so agreeing with the findings for sodium. As before, when no potassium was reported by the gravimetric method, some was recorded by the flame photometer. Again the concordance is better than that between figures for potassium in the same rock determined gravimetrically by different analysts.

CONCLUSIONS

Consideration of the above results indicates that by working with suitably dilute solutions in the presence of an excess of phosphate, the graph of flame intensity *versus* sodium or potassium intensity is sufficiently nearly linear to permit analysis by a direct addition method, the results comparing favourably with those of the classical chemical procedure. The time taken for the analysis of an average sample of acid-soluble rock or mineral, including all preparatory work, is about one hour. If a number of samples are being examined simultaneously, the average time would be less.

All the rocks examined were found to be acid soluble after treatment as described on p. 413, but if the rocks or minerals to be examined are very refractory, *e.g.*, tourmaline, beryl, biotite or topaz, and will not dissolve directly in acid, then, after the Lawrence Smith fusion, the mixture can be extracted with acid and, after the removal of the silica, the sodium and potassium can be determined directly on an aliquot of a measured volume. The presence of large amounts of calcium in the acid solution of the product obtained from the opening-up process will not influence the method in any way when the ammonium phosphate is added in the course of the flame photometry procedure.

If only very small amounts of material are available, it would be possible to use as little as 0·005 g of material if the amount of sodium is above 0·5 per cent., or 0·02 g if the amount of sodium is 0·5 per cent. or less. Hence the method can be used as a micro-method without loss of accuracy.

The authors thank the Directors of the British Drug Houses Limited for permission to publish these results. Thanks are also due to Dr. Max Hey of the British Museum (Natural History) for providing the chemical analyses of the rocks and for helpful discussion.

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ANALYTICAL DEPARTMENT
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A Simple Flame Photometer for Internal-Standard Operation and Notes on Some New Liquid Spectrum Filters

BY (THE LATE) A. M. ROBINSON AND T. C. J. OVENSTON

(*Presented at the meeting of the Physical Methods Group on Friday, October 6th,* 1950)

A flame photometer based on a Dutch design has been built for operation primarily by the internal-standard technique. Two beams, directed simultaneously through "standard" and "sample" spectrum filters respectively, fall on barrier-layer photo-cells whose outputs are balanced potentiometrically by a null-point method.

Special features in the design and operation of this instrument are described, and certain precautions are recommended. The choice of the internal-standard element is briefly discussed.

The transmission characteristics of some new spectrum filters, made by combining layers of solutions of common substances, are given and in some instances compared with those of glass, gelatin and interference filters.

FROM work already published it seems quite clear not only that sodium, potassium and related elements can be determined much more rapidly by means of a flame photometer than by the time-consuming gravimetric procedures, but also that the results so obtained for many materials are quite as reliable. It appears that useful results can be obtained with very simple apparatus in which the excited radiation, after passage through a spectrum filter, falls on a selenium barrier-layer cell connected to a galvanometer. It was desired to explore possible applications of a simple flame photometer of this type, and one described by Boon[1] in 1945 was taken as a model.

Like that of Barnes, Richardson, Berry and Hood,[2] Boon's instrument was designed for direct reading. From the subsequent work of Berry, Chappell and Barnes[3] it appeared that the use of an internal-standard technique and a dual optical system offered certain important advantages, so the design was modified to allow either method of measurement to be used.

DESCRIPTION OF THE FLAME PHOTOMETER

Fig. 1 is a general view of the flame photometer assembly. Cylinder gas is controlled by reducing valves to give a low-pressure supply, pressures being measured by a water manometer. Air from a small compressor is fed through a pressure stabiliser to the atomiser, final pressure being shown by a mercury manometer. The final pressure controls for both gas and air are glass taps that are mechanically connected to slow-motion dials of a type once common on radio sets. Attention is drawn to the cylindrical light shields, which are here shown slid back to reveal the optical assembly. In use these shields are slid forward against the vertical plates on the side limbs of the chimney so that all background radiation other than that from the flame itself is eliminated.

The disposition of the principal parts and the electrical circuit used for the internal-standard method are shown in Fig. 2. The distances between the photo-cells, the lenses and the flame have been chosen as a satisfactory compromise between two opposing effects; greater distances tend to lower the over-all sensitivity, whereas the heat from the flame makes it undesirable to place the photo-cells any nearer. As it is, it is very important to keep the photo-cell shutters up except for the minimum time necessary to make a measurement.

The electrical circuit, except for a minor modification, is that given by Berry, Chappell and Barnes.[3] The filter F′ transmits only the radiation emitted by the internal-standard element, which has been included in known concentration in the sample solution, and the photo-cell C′ receiving this radiation generates a proportional amount of current, which is dispersed along resistance R_2. At the same time the filter F transmits only the radiation emitted by the element being determined and the photo-cell C generates a proportional amount of current, which is dispersed along resistance R_1.

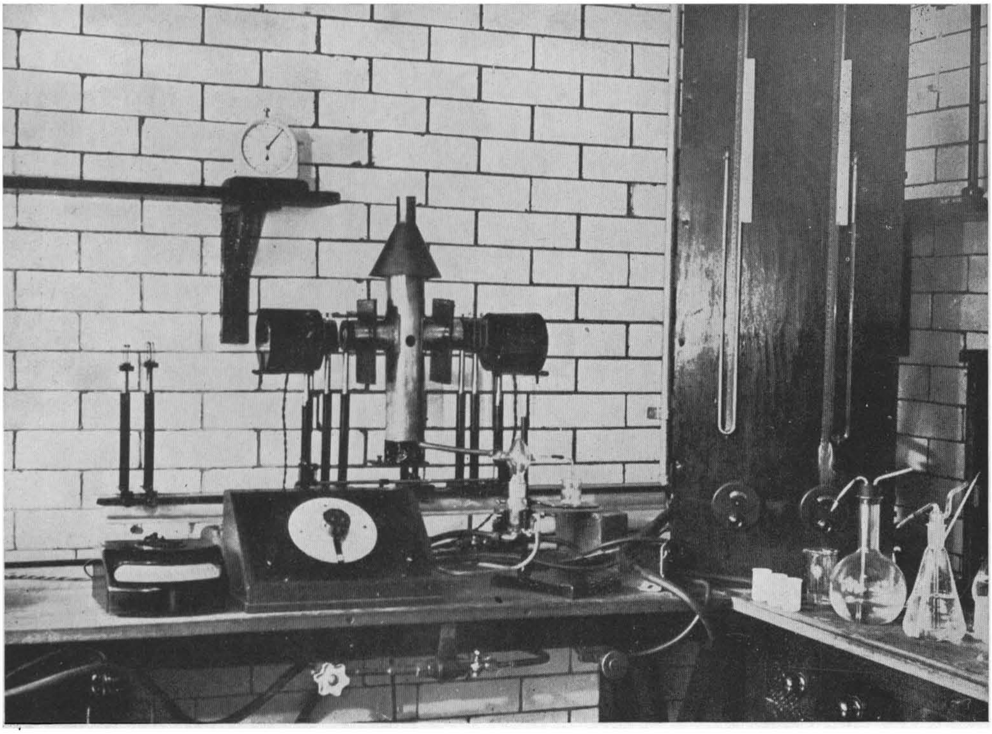

Fig. 1. General view of the flame photometer assembly

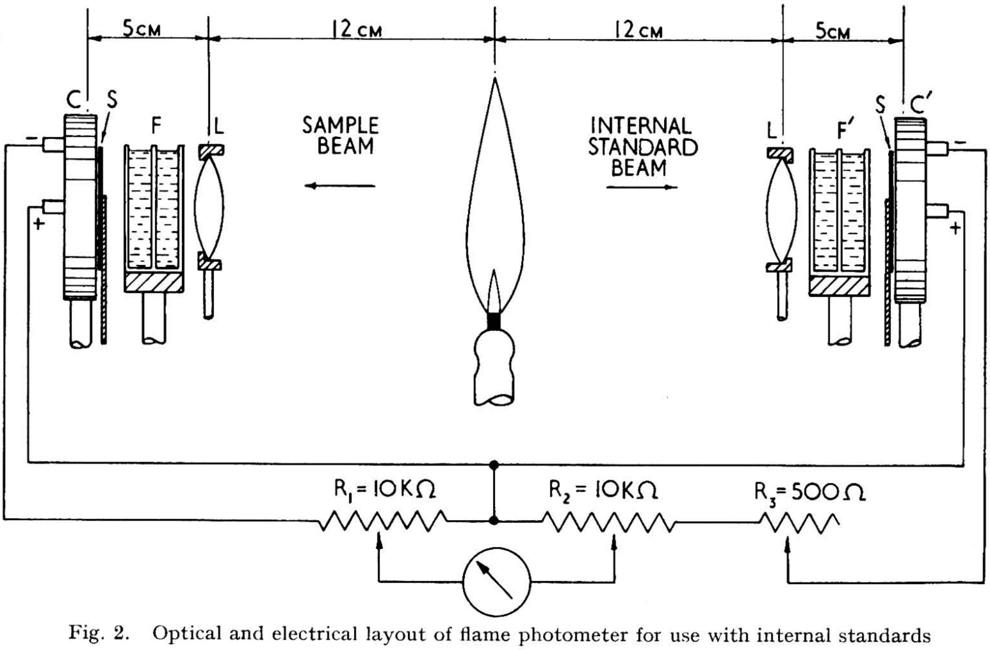

Fig. 2. Optical and electrical layout of flame photometer for use with internal standards

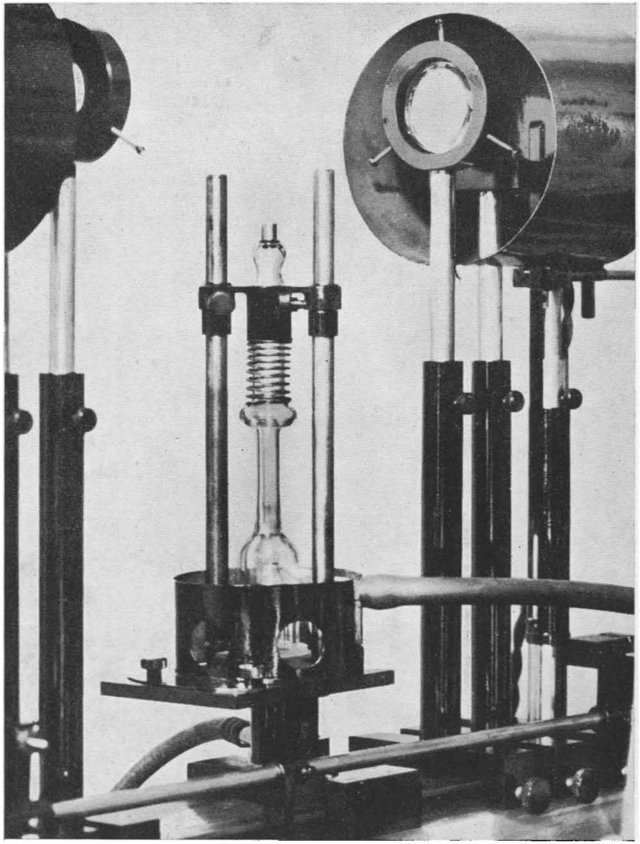

Fig. 3. The burner assembly

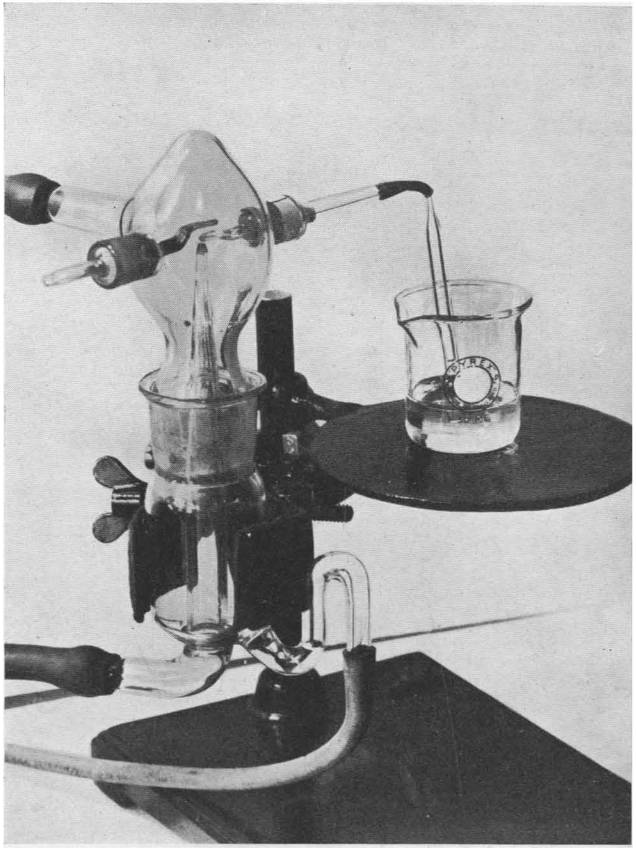

Fig. 4. The atomising vessel

The circuits are balanced by means of a galvanometer, used as a null-point meter, connected to tappings on R_1 and R_2. A Cambridge spot galvanometer with a resistance of 450 ohms was found suitable. Normally, the tapping on R_1 is at the negative end of the resistance so that the whole of the current generated as a result of the emission of the sample element is balanced against the excess of internal-standard current, the range of the determination depending on the latter. Range adjustments can sometimes be conveniently made, however, by moving the galvanometer tapping along R_1, and the exact position can be found again on a subsequent occasion by resetting with the standard solutions. Once set for a given determination, this tapping must not be altered. Resistance R_2 is a precision potentiometer, the galvanometer tapping on which is adjusted by means of the control knob to give no deflection of the galvanometer needle during measurement. The pointer attached to the control knob indicates in degrees the position of the tapping; this value can be related to known concentrations of a given element and hence a calibration graph can be constructed. The small resistance R_3 is useful for making minor adjustments in the course of a long series of determinations when the occasional introduction of standard solutions indicates that a slight drift has occurred.

The burner assembly is shown in Fig. 3. Cylinder gas is passed by way of the lower nozzle into the glass burner, in the body of which it is mixed with air containing the atomised solution passed in by way of the side tube. The base of the burner is pressed against a rubber washer by means of a spring held by an adjustable cross-bar. A short glass tube inserted in the rubber washer is placed over the gas inlet to protect it from the mist. The tip of the burner is a platinum collar 6 mm in diameter.

The atomiser, which is based on the design of Rauterberg and Knippenberg,[4] is shown in Fig. 4. Air is passed in at the bottom under pressure and is forced out of the vertical jet. The horizontal tube leading from the beaker containing the solution is so placed that the air jet, in passing the tip, causes the solution to be sucked into the atomiser, where it is blown against the baffle plate with considerable force. The only outlet for the air is through the side tube to the burner, so that the mist formed in this way is carried along with it. The un-atomised solution falls to the bottom of the vessel, where it syphons to waste. A considerable amount of adjustment is possible by rotation of the jets, both of which are carried on ground-glass joints.

Both atomiser and burner are now obtainable commercially.* They have recently been fully described by Domingo and Klyne,[5] who have adapted Boon's design to the determination of sodium with a selenium photo-cell and of potassium with a caesium photo-cell by the direct method of measurement.

The gas pressure required depends on the size of the nozzle leading into the base of the glass burner. The nozzle size is not critical, but the correct manometer reading for any given nozzle is constant and can be found by reducing the gas flame until it is as non-luminous as possible while at the same time maintaining the flame in a stable condition. The air pressure required depends on the size of the air jet in the atomiser, sufficient air having to be passed to maintain a steady flame. With the type of atomiser described here a pressure of about 40 mm of mercury is usual, the exact value for a given model being found by experiment.

PRECAUTIONS IN OPERATION—

To prevent minor explosions when lighting and extinguishing the burner for use with acetylene - air mixtures, a Y-tube was inserted in the acetylene lead just before it enters the burner. The free end of the Y-tube was permanently connected to a coal-gas supply tap. The coal gas was first turned on and lit. The air supply was then turned on and finally the acetylene. The coal gas was then turned off slowly, care being taken that sufficient acetylene was being supplied to support the flame. Final adjustments were then made in the usual way. When extinguishing the flame, the coal gas was first turned on and the acetylene then turned off. The coal gas was then turned off.

Should a back-fire occur at any time, the burner quickly fills with soot. This soot must be carefully removed before relighting, otherwise the flame may be so unsteady as to be uncontrollable. Even in normal usage of the burner, soot is slowly deposited near the tip; to ensure the best results, this deposit should frequently be removed.

* The apparatus used by the authors was supplied by the Laboratory Glassblowers Co., Valley Works, Lane End Road, Sands, High Wycombe, Bucks.

Another precaution that must be emphasised concerns the close proximity of the photo-cells to the flame. It was found essential in order to prevent fatigue of the photo-cells to keep the shutters closed except for the half minute required for each measurement.

Finally, it was found desirable to avoid taking readings at the moments when the waste in the bottom of the atomiser vessel was syphoning away.

RELATIVE FLAME SENSITIVITIES—

Barnes, Richardson, Berry and Hood[2] preferred a flame with a relatively low temperature because less elements were excited and this made the task of isolating the required radiation simpler. Much sensitivity is lost in this way, however, and many workers prefer the hotter acetylene - air flame. In Fig. 5 are shown the relative sensitivities of acetylene - air, coal gas - air and butane - air flames as indicated by the galvanometer deflection given by various concentrations of sodium. It is clear that excitation in the acetylene - air flame is much greater than in the other two flames and that it should be used whenever sensitivity is of importance.

SELENIUM CELL RESPONSE—

In the present apparatus standard Evans Electroselenium Ltd. (EEL) selenium barrier-layer photo-cells were employed. These show good response over the whole of the visible spectrum and are particularly sensitive in the region near 589 mμ, the wavelength of the sodium doublet. Above 700 mμ, however, the response falls off sharply and small amounts of potassium cannot be determined. For instance, in a direct measurement circuit and with the liquid spectrum filters now recommended, a galvanometer deflection (one-tenth of the full scale) that was given by as little as 0·5 p.p.m. of sodium or 3·2 p.p.m. of lithium required 30 p.p.m. of potassium to reach the same value. For this reason it is usual to measure the potassium emission by means of a caesium photo-emissive cell.

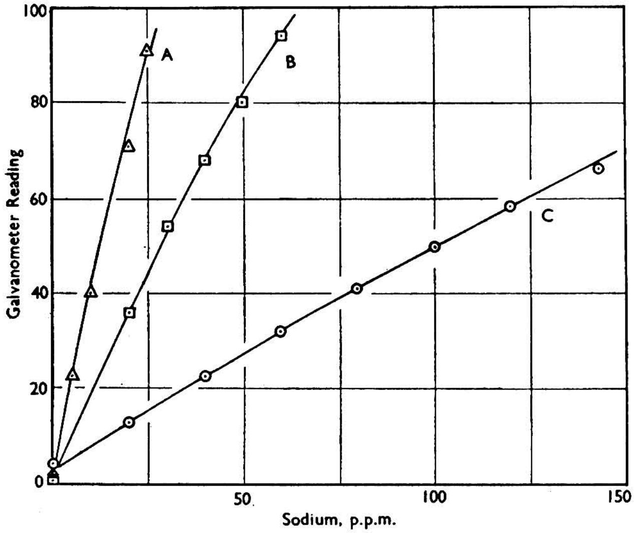

Fig. 5. Relative sensitivities of burner gases
Curve A, acetylene - air; curve B, coal gas - air; curve C, butane - air

For internal-standard work, with two photo-cells in electrical balance, it is desirable to select a type of cell that covers the whole of the working range. Except for work on potassium (and on caesium and rubidium), the selenium cell described above is satisfactory and offers the advantage of cheapness and simplicity. To widen the range it has been the practice, as in the Perkin - Elmer model 52A, to use interchangeable red- and blue-sensitive photo-emissive cells in conjunction with a balanced electronic circuit and high amplification; this, of course, involves considerable expense, and such an apparatus, combined as it is with a dual-prism monochromating system, is possibly as versatile an instrument as can be devised. Since the main body of this paper was written, however, attention has been drawn[6] to the recent production of selenium barrier-layer cells* having a response range extending to about 900 mμ. With these cells it is hoped to extend the range of the present simple assembly to cover all normal requirements.

USE OF INTERNAL STANDARDS

ERRORS AND THE INTERNAL-STANDARD TECHNIQUE—

Errors in flame photometry can be classified into: (*a*) those arising from flame fluctuations; (*b*) those arising from impurities affecting the viscosity or surface tension of the solution, *i.e.*, urea, which depresses, and methanol, which enhances the emission intensity of the alkali metals[3]; (*c*) those arising from the depressing effect of acids and salts[3,7]; (*d*) those arising from inefficiency of the filters.

In the direct (or absolute) method of measurement, flame fluctuations are controlled as much as possible, and it is good practice to alternate samples with standards to detect drift. To cope with the effects of impurities and of large concentrations of salt, a number of suggestions have been made. For example, Berry, Chappell and Barnes[3] have recommended the making up of standards in solutions having the same composition as that containing the element to be determined. This technique is obviously limited to ranges of materials of fairly constant general composition. Shapiro and Hoagland[8] recommend further dilution of samples, by which means the relative effect of these interferences can be very greatly reduced. This dilution technique is certainly effective, but the sensitivity of the determination is, of course, correspondingly reduced. For water analysis, West, Folse and Montgomery[9] have suggested the use of "radiation buffers," that is, concentrated solutions of selected salts added in fixed proportions to the sample solution to buffer any interference from small and variable amounts of these salts.

By means of the internal-standard technique with a dual optical system, errors caused by flame fluctuations, by viscosity and surface tension effects and by the depressing effects of acids and salts are greatly reduced. In addition, any of the suggestions already made to cope with these effects in the direct method of measurement are equally applicable when using the internal-standard technique.

Both methods are dependent on the efficiency of the light filters in cutting off unwanted radiation, but it should be mentioned that it is not necessary for the internal-standard filter to eliminate *all* the radiation of the element being determined, or for the sample filter to eliminate *all* the radiation of the element used as the internal standard, as the calibration graph will take account of this.

It can be concluded that the internal-standard technique can be used with advantage whenever it is appropriate. It is not appropriate unless an internal-standard element can be selected that not only provides a sufficiently strong emission at a convenient wavelength, but also does not occur in appreciable and variable quantities in the material to be analysed.

POSSIBLE INTERNAL-STANDARD ELEMENTS—

Until recently, lithium was the only metal that had been successfully used as an internal standard for flame photometry (excluding spectrographic applications). It is known to be absent from many materials commonly subjected to analysis for sodium and potassium. Eubank and Bogue,[10] however, prefer the direct method for the analysis of Portland cement because this material contains unknown and variable amounts of lithium.

In addition to examining lithium, Berry, Chappell and Barnes,[3] who used a type of photo-cell with a response similar to that of the standard Evans Electroselenium cell, examined the potentialities of rubidium, caesium and indium, but rejected them. The present authors have tried to use the weak emissions available in the blue end of the spectra of rubidium and caesium. Suitable filters were devised, but the concentrations of internal standard required to balance the common alkali metals were far too large to allow the development of practical or economical methods. However, these two metals are sufficiently rare in nature to make them valuable internal-standard elements if it were possible to utilise the radiation of their strong emissions in the near infra-red. It is hoped to give further study to this matter when the new infra-red-sensitive barrier-layer cells have been incorporated in the present apparatus.

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* These cells are manufactured by Megatron, Ltd., London.

Another element worth mention is thallium. This gives a fairly strong emission at 535 mμ, which can be separated completely from the sodium doublet by means of the solution filter whose characteristics are shown in Fig. 9. No further experiments with thallium have yet been made. It should be noted that this metal is toxic and should not be burnt in the flame photometer without an efficient flue.

Finally, it should be mentioned that common elements can sometimes be used as internal standards. One of the authors (A. M. R.) has developed a method for the determination of lithium as a major constituent in magnesium - lithium alloys by using potassium as an internal standard. Sodium and other normal impurities or additions do not interfere and the amount of potassium added as standard is so much in excess of the maximum that could reasonably be expected to be present in these alloys that their true potassium content is of no account. The weak photo-cell response at 766 to 770 mμ is then an advantage; in fact, with an infra-red-sensitive photo-cell it would be necessary to reduce the intensity of the standard beam by means of an iris diaphragm or similar device. This method will be described in a separate paper.

FILTERS

For filtering the radiation, glass or gelatin filters are undoubtedly very convenient to use, but they are not particularly efficient. In addition, gelatin filters are apt to change their transmission characteristics with use. It is considered preferable to use cells filled with solutions of known transmission characteristics. These are readily made up and can always be relied on.

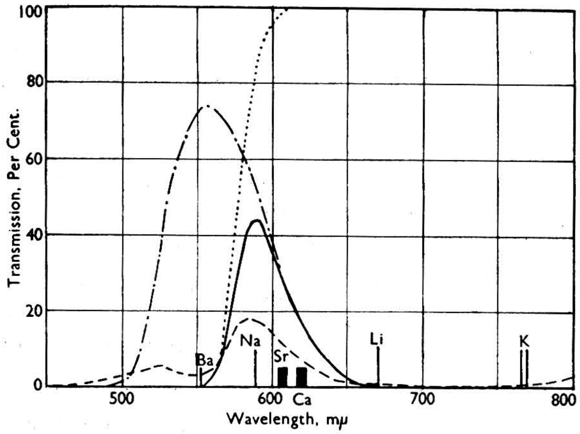

Fig. 6. Transmission curves for sodium filters

———— Complete liquid filter
.... Sodium dichromate component
·—·—·— Cupric chloride component
– – – – – Chance OY1 and Ilford 803 combined

With two layers of solutions it is possible to devise combinations that completely stop all radiations outside a limited range of the spectrum. For example, potassium dichromate has a very sharp cut-off that can be varied over about 50 mμ by changes of concentration. By using sodium dichromate, higher concentrations are possible and radiation shorter than that emitted by sodium can be readily cut off.

The transmission curve of a 1-cm layer of an aqueous 50 per cent. w/v solution of sodium dichromate dihydrate ($Na_2Cr_2O_7.2H_2O$) is shown in Fig. 6, together with the corresponding curve for a 5·0 per cent. w/v solution of cupric chloride dihydrate ($CuCl_2.2H_2O$) in 8 N hydrochloric acid. By combining these two layers in series they form an efficient filter for sodium radiation with transmission characteristics indicated by the continuous curve in Fig. 6. This filter cuts off all radiation in the photo-cell range of wavelengths from 553 mμ downwards and from 671 mμ upwards, and transmits 44 per cent. of the sodium radiation at 589 mμ. Potassium, lithium (at 671 mμ) and barium radiation are efficiently stopped. Calcium and strontium band emissions, which are most intense at about 620 mμ and 605 mμ, respectively, are partly transmitted. The weak lithium emission at 610 mμ is within the transmission range of this filter; fortunately, the effect of this is noticeable only when the concentration of lithium is high and, in any event, could not contribute an error when lithium is used as an internal standard, though it would increase the size of the blank measured when no sodium is present.

The pecked curve in Fig. 6 shows the transmission spectrum of the combination of a Chance OY1 glass filter with an Ilford 803 gelatin filter, a system that has been recommended for the isolation of sodium radiation. The system transmits 18 per cent. of the sodium radiation and a correspondingly reduced proportion of the calcium and strontium radiation. Its use would, therefore, reduce the sensitivity for sodium to less than half of that obtained with the liquid filter combination, although the interference to be expected from calcium and strontium is no less. In addition, transmission down to about 490 mμ is appreciable, in which region the barium emission at 553 mμ and various barium oxide bands at lower wavelengths occur.

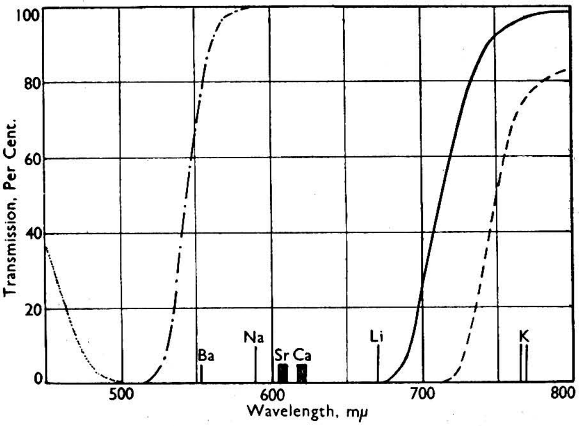

Fig. 7. Transmission curves for potassium filters

———— Complete liquid filter

.... Aniline blue component (this coincides with that for the complete filter above 500 mμ)

·–·–·– Potassium dichromate component

– – – – – Ilford 207

In Fig. 7 the transmission curves of a liquid filter for potassium and of Ilford 207 gelatin filter are compared. The liquid filter combination consists of 1-cm layers of a 2 per cent. w/v aqueous solution of potassium dichromate ($K_2Cr_2O_7$) and a 0·02 per cent. w/v solution of aniline blue in 95 per cent. ethanol. The cut-off is due entirely to the aniline blue solution. The purpose of the dichromate layer is to prevent transmission below 500 mμ, which would be permitted by a region of low absorption by the aniline blue solution. The concentration of the aniline blue solution has been selected so that all radiation at 671 mμ and below is stopped. At the same time, 96 per cent. of the potassium radiation at 766 mμ and 770 mμ is transmitted, as compared with 75 per cent. for the Ilford 207 filter. The Ilford 207 filter, however, is also very efficient in stopping unwanted radiation. Radiation from elements emitting at lower energy levels is cut off by the limiting response of the photo-cells in the infra-red. With photo-cells more sensitive to infra-red radiation it would be necessary to devise a filter to stop the lithium emission at 831 mμ, the rubidium emissions at 780 mμ and 795 mμ and the caesium emissions at 852 mμ and 894 mμ, should these elements be present in appreciable quantities.

The liquid filter combination for lithium, Fig. 8, consists of 1-cm layers of a 0·2 per cent. w/v solution of rhodamine B in water and a 1·0 per cent. w/v solution of cupric chloride dihydrate in 8 *N* hydrochloric acid. This combination has been designed to stop radiation at 620 mμ and below and at 766 mμ and above, and is thus highly efficient in isolating the lithium radiation, which is transmitted to the extent of 25 per cent.

The liquid filter proposed for thallium, Fig. 9, consists of 1-cm layers of a 0·5 per cent. w/v aqueous solution of potassium dichromate and a 100 per cent. w/v solution of cupric nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) in 2 *N* nitric acid. The combination transmits 21 per cent. of the thallium radiation at 535 mμ, while the presence of large amounts of sodium causes no appreciable increase in the total amount of transmitted radiation. Barium and barium oxide radiation and some of the calcium oxide radiation at 550 to 555 mμ is partly transmitted.

The effect of increasing the optical thickness of a liquid filter is of interest. It is well known that an increase in the optical path of a homogeneous absorbing medium by a factor of f will have the effect of reducing the transmission by raising it to the power of f. It follows that the efficiency of a liquid filter may be continuously increased by increasing its thickness, for the smaller the transmission the greater will be the reduction in transmission. Hence, where a transmission of 50 per cent. would fall to 25 per cent. on doubling the thickness of the filter, a transmission of 25 per cent. would fall to 6·25 per cent. and one of 10 per cent. to 1 per cent. In Fig. 10, curve A shows the transmission spectrum of the normal-thickness sodium filter already described and curve B shows that of the same filter made up of two 2-cm layers. The increase in efficiency is evident, for while the transmission of the sodium radiation has fallen from 44 per cent. to 19·4 per cent., the transmission of the strontium radiation at 605 mμ has been reduced more than threefold and that of the calcium radiation at 620 mμ has been

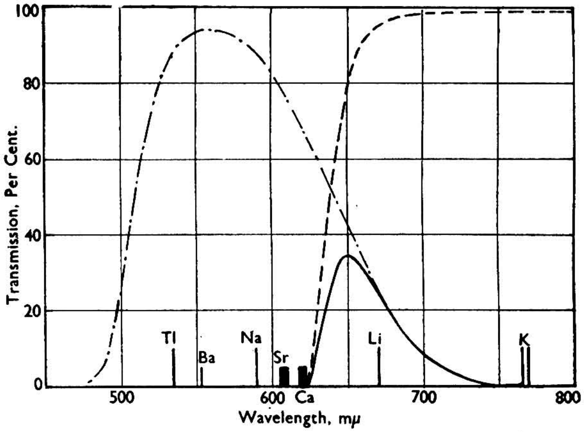

Fig. 8. Transmission curves for the lithium filter

———— Complete liquid filter
– – – – – Rhodamine B component
· — · — · — Cupric chloride component

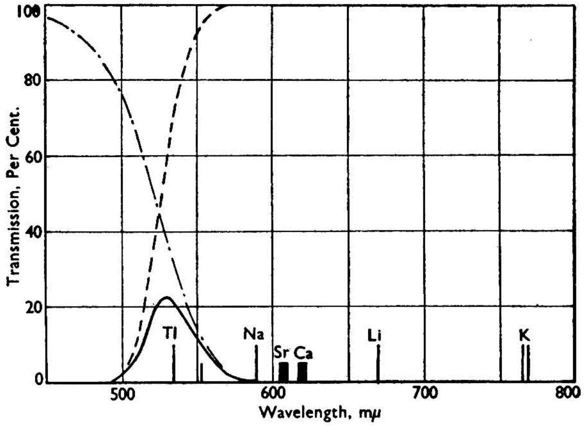

Fig. 9. Transmission curves for the thallium filter

———— Complete liquid filter
– – – – – Potassium dichromate component
· — · — · — Cupric nitrate component

reduced sevenfold. By continuing this process it is possible to obtain an almost perfect monochromatic filter. Unfortunately, with each reduction of maximum transmission the sensitivity of the determination is correspondingly decreased, and the problem resolves itself into choosing the most suitable compromise to meet any particular set of requirements.

For comparison, the transmission spectrum of a typical interference filter of maximum transmission at 589 mμ is shown in Fig. 10 as curve C. This curve was calculated from the manufacturer's data sheet and may be slightly optimistic, but there is no doubt that the efficiency of these somewhat costly filters is very good. It should be noted, however, that the maximum efficiency of an interference filter can only be attained when the transmitted beam consists of absolutely parallel radiation. For this reason the present optical lay-out is not considered suitable for use with these filters. By replacing the existing lenses by double lens systems designed so that the rays emanating from the centre of the flame are parallel when passing between the two parts of each lens system, it should be possible to use interference filters in the present apparatus by inserting them in this part of the beam. The comparatively large flame area, however, makes it impossible to obtain a completely parallel beam.

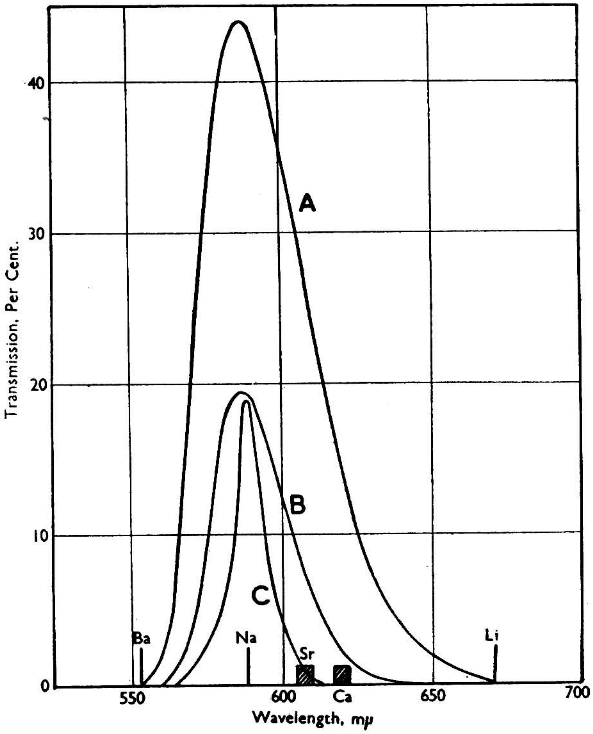

Fig. 10. Transmission curves showing the effect of increasing the optical depth of the sodium liquid filter and a comparison with an interference filter.

Curve A, normal sodium filter, 1 cm + 1 cm; curve B, double thickness sodium filter, 2 cm + 2 cm; curve C, typical interference filter (parallel beam)

We acknowledge the helpful advice given by Dr. E. J. Bowen and Dr. L. Leyton, and also thank Dr. Bowen and Mr. L. G. Young for the loan of certain components of the first assembly.

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The Determination of Aluminium in Copper-Base Alloys

BY G. W. C. MILNER* AND J. TOWNEND

A method for the determination of aluminium in brasses by the selective precipitation of aluminium as its benzoate complex has been studied and modified to enable the accurate determination of this element in all types of copper-base alloys. The alloy is dissolved in nitric acid, tin is removed by filtration and then the pH of the solution is adjusted to the region of pH 4. Copper and iron are then reduced by boiling with hydroxylamine hydrochloride and the aluminium is selectively precipitated by the addition of ammonium benzoate. After filtration, the aluminium benzoate is dissolved in a hot ammoniacal tartrate solution, re-precipitated as aluminium oxinate and the determination completed volumetrically.

The range of the method is from 0·1 per cent. to approximately 12 per cent. of aluminium.

THE older methods for the determination of aluminium in copper-base alloys involve the following time-consuming processes: removal of the copper by precipitation as sulphide or by electrolysis, precipitation of aluminium and iron hydroxides together, re-solution of the precipitate in hydrochloric acid after filtration and then selective precipitation of aluminium hydroxide by means of sodium thiosulphate.[1,2]

Later methods fall into two main groups according to whether they do or do not involve a preliminary separation of the aluminium from the other alloying constituents by electrolysis with a mercury cathode. This electrolytic procedure gives virtually complete deposition of copper, zinc, iron and nickel, but only partial deposition of manganese,[3] and since this element interferes in the subsequent method for determining aluminium, an additional step is necessary to separate it from the aluminium. The results of the determination of aluminium by this type of procedure are very reliable,[4] but in the analysis of many samples in an inspection laboratory the electrolytic procedure can delay the determinations; it also yields large quantities of highly contaminated mercury that must subsequently be purified; for this reason the A.S.T.M. method[5] incorporates a mercury-cathode electrolysis *after* the copper has been deposited electrolytically on a platinum cathode.

In the group of methods that do not use mercury-cathode electrolysis is that of Edwards,[6] who recommends an 8-hydroxyquinoline procedure for the determination of aluminium in aluminium bronzes that makes use of potassium cyanide to suppress the interference of copper, iron and nickel, and ferrocyanide to remove zinc and manganese as insoluble precipitates. This method, however, is not applicable to brasses. A method proposed by Bayley[7] for the determination of aluminium in brasses makes use of ammonium benzoate as a direct selective precipitant for aluminium after the reduction of copper and iron with hydroxylamine hydrochloride.

As there is a real need of a purely chemical procedure that is both rapid and accurate and that is applicable to the determination of aluminium in many types of copper-base alloys, the benzoate precipitation procedure was studied to find if it would meet this need.

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EXPERIMENTAL

According to Smales,[8] the pH range for the precipitation of aluminium benzoate is from 3·5 to 5, with an optimum pH of about 4. In Bayley's method the pH is adjusted to this region by the addition of diluted ammonium hydroxide (1 + 1) to a nitric acid solution of 0·5 g of the brass to give the first permanent precipitate of cupric hydroxide. This precipitate is then just cleared by the careful addition of diluted hydrochloric acid (1 + 4). The solution is brought to the boil and 20 ml of a 2 per cent. solution of hydroxylamine hydrochloride containing 2 per cent. of ammonium hydroxide and 10 per cent. of ammonium chloride is added to reduce the copper completely. The aluminium is then precipitated by the addition of 10 ml of a 10 per cent. solution of ammonium benzoate, filtered on a paper-pulp pad after digestion for 5 minutes and washed with 1 per cent. ammonium benzoate solution. The aluminium benzoate precipitate is dissolved in a hot ammoniacal tartrate solution, the aluminium re-precipitated as its oxinate and finally determined volumetrically in the usual way.

This method applied to the determination of aluminium in a number of standard and synthetic brasses gave good results for amounts of aluminium less than 1·0 per cent., but for amounts in the region of 2 per cent. the results were from 5 to 10 per cent. below the amount present. On occasions it was observed that the aluminium precipitated as the hydroxide instead of as the benzoate; when this occurred the determinations were rendered invalid because of the insolubility of aluminium hydroxide in the ammoniacal tartrate solution. It was considered desirable to apply a more effective buffering action in the requisite pH region to prevent any aluminium precipitating as hydroxide. The above method was therefore modified by the addition of 50 ml of a pH 4·2 buffer solution (4·1 g of sodium acetate and 35 ml of *N* hydrochloric acid, diluted to 250 ml) after the removal of the cupric hydroxide precipitate with dilute hydrochloric acid; the method was then applied to a number of brass samples. Although all the precipitates then had the granular form of the benzoate, the results for the higher amounts of aluminium were still low.

Other possible sources of error were next investigated. The aluminium benzoate precipitate was allowed to digest hot for longer times of up to 30 minutes before filtration. The precipitate was also washed with a solution of ammonium benzoate adjusted to pH 4 by the addition of acetic acid. But the results for samples containing 2 per cent. of aluminium were still 3 to 5 per cent. below the amount present. In the penultimate operation the aluminium oxinate is dissolved from a fairly large paper-pulp pad with hydrochloric acid, and the low results could conceivably be caused by the incomplete extraction of the oxinate from the paper pulp. However, it was found that complete extraction was always attained on applying the same technique to known amounts of aluminium oxinate filtered on similar sized paper-pulp pads. The difficulty was eventually overcome by increasing the volume of 10 per cent. ammonium benzoate solution used to precipitate the aluminium from 10 to 20 ml, and with this modification results for four different synthetic brasses each containing 2·00 per cent. of aluminium were 2·01, 1·99, 1·99 and 2·00 per cent. It appears, therefore, that the low results for aluminium by Bayley's method were due either to the incomplete precipitation of the benzoate or to some aluminium being precipitated as the hydroxide instead of the benzoate, or to a combination of both.

This method, incorporating the use of the pH 4·2 buffer and 20 ml of 10 per cent. ammonium benzoate precipitant, was next applied to the determination of aluminium in aluminium bronzes containing approximately 10 per cent. of aluminium, starting with samples weighing 100 mg so as to give suitable titres in the volumetric finish. In every experiment the aluminium was precipitated as the hydroxide instead of as the benzoate, so making the determination completely useless. As in these samples there was only about 90 mg of copper compared with approximately 300 mg in brass samples, it was considered essential to reduce the amount of the hydroxylamine reagent; on using 6 ml of the hydroxylamine reagent on a synthetic bronze containing 10 per cent. of aluminium, 9·10 per cent. was found. These results indicated that the method developed for brasses is applicable only to types of alloys containing a fixed proportion of copper; before it can be satisfactorily applied to alloys containing differing amounts of copper, the amount of hydroxylamine reagent to be added must be accurately related to the amount of copper present. As the aim of this investigation was to develop a single method suitable for the determination of aluminium in all types of copper-base alloys, it was desirable to reconstruct the method completely.

As the reduction of copper by hydroxylamine hydrochloride proceeds, the solution becomes increasingly acid, so that, even on starting with an aqueous solution of copper sulphate, the acidity of the solution eventually increases sufficiently to prevent further reduction and the copper is incompletely reduced. In Bayley's method the ammonia present in the hydroxylamine reagent neutralises this developed acidity and so allows the complete reduction of the copper. But for a method of general application it seemed better to use a pure solution of hydroxylamine hydrochloride and a pH 4 buffer of such capacity that at least 500 mg of copper could be reduced without a change of pH. A series of tests was performed on 500-mg amounts of copper, the amounts of sodium acetate and hydrochloric acid used in the pH 4·2 buffer being increased by the same factor to give buffers of approximately the same pH, but of increasing buffering action. The results of the tests are shown in Table I.

TABLE I

CHOICE OF BUFFER SOLUTION FOR COPPER REDUCTION

Ratio of sodium acetate (g) to *N* hydrochloric acid (ml)	Observations
0·82/7	Copper incompletely reduced
2/17	Copper incompletely reduced
3/25·5	Copper incompletely reduced
4·1/35·5	Copper completely reduced, but pH reduced below 4
5/42·7	Copper completely reduced, but benzoate precipitate gelatinous
7·5/64	Copper completely reduced and benzoate precipitate filterable

It was further found that 15 ml of 5 per cent. hydroxylamine hydrochloride solution was just sufficient to reduce 500 mg of copper. With this quantity of hydroxylamine hydrochloride and 7·5 g of anhydrous sodium acetate dissolved in 64 ml of *N* hydrochloric acid as buffer, the method was applied to synthetic alloys with the results shown in Table II.

TABLE II

RESULTS ON SYNTHETIC ALLOYS WITH THE CHOSEN BUFFER

Composition of alloy			Aluminium found, mg
Copper, mg	Aluminium, mg	Iron, mg	
500	10·00	nil	10·02
100	10·00	nil	10·04
100	10·00	10	10·02

Although a good result was obtained with the alloy containing iron, a slight brown turbidity remained after the copper reduction, and the oxinate precipitate was discoloured. This behaviour was possibly due to the formation of a basic acetate of iron; the effect was avoided by adding the hydroxylamine hydrochloride to the cold solution of the alloy and then heating to boiling. The final method is given below.

METHOD

The following method is applicable to coppers, brasses and aluminium bronzes for samples that contain the equivalent of 0·5 g or less of copper. The range of the method is from 0·1 per cent. to approximately 12 per cent. of aluminium.

REAGENTS—

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

Nitric acid, 0·5 per cent.—Dilute 0·5 ml of concentrated nitric acid (sp.gr. 1·42) to 100 ml with water.

Hydrochloric acid, diluted (1 + 4)—Dilute 20 ml of concentrated hydrochloric acid (sp.gr. 1·16) to 100 ml with water.

Buffer solution—Dissolve 75 g of powdered anhydrous sodium acetate in 640 ml of *N* hydrochloric acid.

Hydroxylamine hydrochloride, 5 per cent. solution—Dissolve 5 g of solid reagent in 100 ml of water.

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 benzoate wash solution, 1 *per cent.*—Prepare by dilution from the 10 per cent. solution.

Ammoniacal tartrate solution—Dissolve 25 g of tartaric acid in water, add 120 ml of ammonium hydroxide (sp.gr. 0·880) and 5 g of potassium cyanide, and dilute to 1 litre with water.

8-*Hydroxyquinoline,* 2 *per cent. solution*—Dissolve 5 g of solid reagent in 15 ml of glacial acetic acid and dilute to 250 ml with water.

Potassium bromate, 0·1 N *solution*—Dissolve 2·7840 g of potassium bromate and 15 g of potassium bromide in water and dilute to 1 litre.

Sodium thiosulphate, approximately 0·1 N *solution*—Dissolve 25 g of sodium thiosulphate crystals in water and make up to 1 litre.

Potassium iodide, 15 *per cent. solution*—Dissolve 15 g of solid reagent in 100 ml of water.

Starch, 0·5 *per cent. solution*—Make 0·5 g of soluble starch into a paste with a few millilitres of water and add to 100 ml of boiling water. Cool.

PROCEDURE—

Weigh an amount of sample according to the percentage of aluminium in the sample as follows—

For aluminium contents less than 2·0 per cent., weigh out 0·5 g.
For aluminium contents from 2·0 to 4·0 per cent., weigh out 0·25 g.
For aluminium contents greater than 4·0 per cent., weigh out 0·1 g.

Transfer the weighed sample to a 400-ml conical beaker, dissolve it in 5 ml of concentrated nitric acid (sp.gr. 1·20), add approximately 10 ml of water and boil to remove nitrous fumes. If tin is present in the sample, evaporate the solution to a paste, re-dissolve the salts in about 15 ml of 0·5 per cent. nitric acid and filter through a small, tight, paper-pulp pad. Wash well with approximately 50 ml of hot 0·5 per cent. nitric acid and collect the filtrate and washings in a 400-ml conical beaker. If tin is absent, dilute the sample solution, after removing the nitrous fumes, to approximately 75 ml with water.

Carefully add diluted ammonium hydroxide (1 + 1) to give the first permanent precipitate and then add diluted hydrochloric acid (1 + 4) dropwise to just clear the precipitate. Add 70 ml of buffer solution and 15 ml of hydroxylamine hydrochloride solution, and heat to boiling. Boil for one minute, then remove from the hot-plate and add 20 ml of 10 per cent. ammonium benzoate solution in one rapid addition. Stand the solution by the side of the hot-plate for about 15 minutes to allow the aluminium benzoate precipitate to settle and the supernatant liquid to become perfectly clear.

Filter through a fairly large paper-pulp pad of medium compactness* and wash the precipitate and precipitation beaker well with hot ammonium benzoate wash solution. Remove surplus liquid from the pad by suction and carefully transfer the pad and precipitate to the precipitation beaker. Wash the funnel with 50 ml of hot ammoniacal tartrate solution and then with hot water, and collect the washings in the precipitation beaker. Dilute to about 150 ml with water and digest at 80° to 90° C for a few minutes to dissolve the precipitate. Then precipitate the aluminium oxinate by addition of 20 ml of 8-hydroxyquinoline solution with constant shaking. Replace the beaker on the hot-plate and maintain the solution at 80° to 90° C until the supernatant liquid becomes quite clear. Filter through a small loosely-packed paper-pulp pad and wash the precipitate well with cold 5 per cent. ammonium hydroxide solution and finally wash once with cold water.

Transfer the filter funnel to the neck of a 500-ml glass-stoppered bottle. Add 40 ml of hot (80° C) concentrated hydrochloric acid (sp.gr. 1·16) to the precipitation beaker to dissolve traces of aluminium oxinate, and then dissolve the precipitate from the pad into the bottle with this acid. Wash the beaker and pad well with hot water. Dilute the final volume of solution in the bottle to 200 ml with water and cool. Add a few drops of methyl red indicator solution and run in the bromate - bromide solution with constant shaking until the colour changes from orange to yellow. Add 4 ml of bromate - bromide solution in

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* It is important not to make this pad too large, otherwise at the filtration stage of the aluminium oxinate the amount of pulp is too great to facilitate efficient washing of the precipitate. Thin and loosely packed pads, however, often allow the aluminium benzoate to pass through; the ideal size can only be determined satisfactorily by experience with the method.

excess and then 10 ml of potassium iodide solution. Mix well and titrate with sodium thiosulphate solution until the brown-coloured precipitate just clears. Then add about 5 ml of starch solution and continue the titration until one drop of thiosulphate turns the solution bright yellow.

STANDARDISATION OF THE SODIUM THIOSULPHATE—

With a pipette, place 25·0 ml of the bromate - bromide solution in a glass-stoppered bottle and add 10 ml of potassium iodide solution, 125 ml of water and 40 ml of concentrated hydrochloric acid (sp.gr. 1·16). Mix well and then titrate with the thiosulphate solution, using starch as indicator, to the disappearance of the blue colour.

If x ml of thiosulphate are needed, the factor (f) of the thiosulphate is $25/x$.

CALCULATION OF RESULTS—

If b = the volume in millilitres of the bromate - bromide solution added,
t = the volume in millilitres of the thiosulphate solution added
and f = the factor of the thiosulphate solution,

then the percentage of aluminium $= \dfrac{b - t \times f}{(\text{weight of sample in g})} \times 0{\cdot}022475$

RESULTS

Excellent recoveries of known amounts of aluminium added to pure copper have already been reported above for this method. The possible interfering effects of the alloying elements usually present in copper-base alloys were next studied by adding known amounts of pure aluminium to a typical alloy brass and then determining the total aluminium by the recommended procedure. The brass used had a percentage composition of: Cu, 55·66; Sn, 1·30; Ni, 2·85; Fe, 0·97; Mn, 0·17; As, 0·20; Al, 0·48; Zn, remainder; volumes of a standard aluminium solution were added to increase the aluminium percentage by 0·5 and 1·0 per cent. respectively. The recoveries of aluminium under these conditions are shown in Table III.

TABLE III

RECOVERY OF ALUMINIUM ADDED TO A STANDARD ALLOY

	Aluminium present, %	Aluminium recovered, %
Sample only	0·48	0·48
	0·48	0·48
Sample + 0·50% of aluminium	0·98	0·99
	0·98	0·985
Sample + 1·0% of aluminium	1·48	1·49
	1·48	1·49

As the results of these experiments suggested that interference from the usual alloying constituents of copper-base alloys was negligible, the procedure was applied to the determination of aluminium in different types of alloys with the results shown in Table IV.

TABLE IV

DETERMINATION OF ALUMINIUM IN ALLOYS OF KNOWN COMPOSITION

	Composition, %								Aluminium by recommended method, %
Type of alloy	Cu	Pb	Fe	Mn	Sn	Ni	Zn	Al	
Aluminium bronzes—									
(*a*) Highly alloyed ..	79·58	—	4·51	1·03	0·005	5·11	0·005	9·72*	9·70
(*b*) Nickel absent ..	84·90	—	3·15	1·92	0·14	—	0·80	9·17*	9·23
(*c*) Low manganese ..	83·17	—	3·33	0·17	0·005	3·93	0·05	9·32*	9·33
Brasses—									
(*a*) 60/40 type	56·08	0·92	2·01	0·28	—	—	Rem.	0·35†	0·35
(*b*) B.C.S. "B"	58·8	0·78	0·91	1·03	1·75	1·01	33·9	1·62†	1·56
(*c*) Propeller metal ..	55·75	0·06	0·87	0·23	1·17	0·005	Rem.	0·21†	0·19
(*d*) Aluminium brass ..	77·86	0·02	0·02	—	0·02	0·03	20·0	1·99†	1·96

* By a mercury cathode electrolysis method.[4] † By gravimetric analysis.[1,2]

This procedure is fairly rapid, as a single determination takes only about two hours. Moreover, the results obtained for aluminium in different types of copper-base alloys have been found to be reliable and in good agreement with the results obtained by classical methods of analysis. The procedure is, therefore, ideal for the inspection analysis of copper-base alloys.

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BRAGG LABORATORY
NAVAL ORDNANCE INSPECTION DEPARTMENT
JANSON STREET, SHEFFIELD, 9

November, 1950

Notes

MILK SOLIDS IN ICE-CREAM: A SORTING TEST

THE Food Standards (Ice-Cream) Order, 1951, requires that ice-cream shall contain, among other constituents, 7½ per cent. of milk solids other than fat. It has furthermore been made clear by the Ministry of Food that the expression "milk solids other than milk fat" means the total solids normally present in skimmed milk.

Although the determination of lactose and ash may be a useful guide to the proportion of milk solids other than fat present in ice-cream, it does not exclude the possibility that the milk solids may have been added in the form of whey powder and not as skimmed milk solids containing a full complement of milk protein. In order to preclude this possibility when examining samples of ice-cream, it is necessary to determine the casein content, and indeed it is now our experience that the casein present in ice-cream gives the best measure of the proportion of milk solids other than milk fat that are present.

The method usually employed for the determination of casein in the presence of other protein materials consists in extracting the material with a 3 per cent. solution of sodium oxalate, the casein thereby dissolved being subsequently precipitated by the addition of acetic acid. When applied to ice-cream, however, this method has been found to be rather lengthy, in that with some samples considerable difficulty has been experienced in obtaining a clear filtrate after treatment with sodium oxalate, and indeed any method involving a Kjeldahl determination of nitrogen is to be avoided in a sorting method whenever possible.

Accordingly a search was made for a more rapid method for the determination of casein that might form the basis of a routine sorting test.

A study of the proteins that are likely to be present in ice-cream showed that casein, the principal protein in milk, contained considerably more tryptophan than any other protein and it therefore appeared to us that the determination of the tryptophan in ice-cream might well form the basis of a sorting test.

Various methods have been suggested in the literature for the determination of tryptophan in casein, and from a study of these it was considered that the method of May and Rose,[1] which was subsequently modified by Sullivan, Milone and Everett,[2] might prove suitable for the purpose. This method consists in hydrolysis of the protein with hydrochloric acid followed by treatment with *p*-dimethylaminobenzaldehyde reagent, which in the presence of tryptophan gives a blue coloration. Accordingly tests were made with synthetic mixtures containing sugar, margarine, skimmed milk powder and water, and as the result of these experiments the following procedure was devised.

METHOD

REAGENTS—

p-*Dimethylaminobenzaldehyde solution*—Dissolve 5 g of *p*-dimethylaminobenzaldehyde in 100 ml of 10 per cent. v/v sulphuric acid.

Dilute hydrogen peroxide solution—Dilute 10 ml of 3 per cent. (10-volume) hydrogen peroxide to 100 ml with distilled water.

Diluted hydrochloric acid—Concentrated hydrochloric acid diluted with an equal volume of water.

PROCEDURE—

Weigh 2 g of ice-cream in a 100-ml beaker, add 15 ml of water, boil gently to dissolve the starch and then cool. Precipitate the casein by the addition of 0·06 g of tannic acid, 0·5 ml of acetic acid, B.P., and 0·1 g of sodium chloride; stir, allow to stand for five minutes or until the precipitate has coagulated, and filter through a Whatman No. 4 filter-paper. Wash the precipitate thoroughly with warm water, macerating or stirring the precipitate in order to assist the washing out of the carbohydrates. Remove the fat by washing first with acetone and then with ether. Pierce the bottom of the filter-paper with a glass rod and wash the precipitate into a 100-ml beaker with 50 ml of diluted hydrochloric acid (1 + 1). Place the beaker in a water-bath at 90° C for 10 minutes, then add 0·5 ml of *p*-dimethylaminobenzaldehyde reagent and return to the water-bath for a further 30 minutes. Remove the beaker from the water-bath, add 0·3 ml of dilute hydrogen peroxide solution and allow the blue colour to develop for at least 30 minutes. Make the solution up to 50 ml, filter and measure the blue colour in a colorimeter or absorptiometer in a 1-cm cell.

Prepare a standard graph by taking 0·05, 0·1, 0·15, 0·2 and 0·3-g quantities of skimmed milk powder, the protein content of which has been previously determined, and treating them by the procedure described above for 2 g of ice-cream. From the graph so obtained, the quantity of milk solids other than milk fat in the sample may be readily calculated.

Experience has shown that the reaction between *p*-dimethylaminobenzaldehyde and tryptophan is inhibited by the presence of carbohydrates, which give a brown colour with the reagent if they are not properly removed as described in the procedure. Traces of fat do not interfere with the reaction but larger quantities remain behind as an insoluble precipitate after treatment with hydrochloric acid and tend to slow up the development of the full blue colour. Substantial quantities of wheaten flour do not interfere with the test provided the carbohydrate is removed as described above. The only natural substances so far encountered that interfere in any way with the test are soya flour and cocoa. Soya flour gives a blue colour, but the colour developed from a given weight is considerably less than that given by an equal weight of skimmed milk solids. Cocoa interferes owing to a deep reddish-brown coloration obscuring any blue colour due to casein. This unfortunately makes the test of little value with "choc-ices" unless it is possible to separate completely the chocolate from the ice-cream.

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G. F. J. HART

DR. BERNARD DYER AND PARTNERS
LONDON, E.C.3

May, 1951

3:3′-DIMETHYLNAPHTHIDINE AS A REAGENT FOR THE DETECTION OF VANADIUM

THE use of 3:3′-dimethylnaphthidine (3:3′-dimethyl-4:4′-diamino-1:1′-dinaphthyl) as a reagent for the detection of small amounts of zinc has been described in a previous communication.[1] This test depends ultimately on the oxidation of the reagent to an intense red - violet product by the ferricyanide ion. As would be expected, other oxidising agents behave similarly.

We have determined the sensitivities of three of the commoner oxidising agents (Cr_2O_7'', MnO_4' and VO_3') and the results are shown below—

Ion	Limit of identification	Concentration limit
Cr_2O_7''	0·1 µg	1 in 500,000
MnO_4'	0·5 µg	1 in 100,000
VO_3'	0·1 µg	1 in 500,000

Recently, Belcher and Nutten[2] have determined the sensitivities toward oxidising agents of several substituted benzidines and related compounds. Some of these reagents were slightly more sensitive than 3:3′-dimethylnaphthidine towards Cr_2O_7'' and MnO_4', but only one, 2:7-diaminofluorene, was as sensitive towards VO_3'. The colour given by 3:3′-dimethylnaphthidine and Cr_2O_7'' or MnO_4' faded after about 30 minutes, but that given by VO_3' showed no diminution in colour after standing for 24 hours. The colour given by 2:7-diaminofluorene and VO_3' faded shortly after development; hence 3:3′-dimethylnaphthidine is the most suitable amine of those examined for the detection of VO_3'.

Meaurio[3] has previously recommended diphenylamine for the detection (and colorimetric determination) of VO_3'. We have compared this reagent with 3:3′-dimethylnaphthidine, but the colour fades in a few minutes and the sensitivity is only 10 µg.

METHOD—

Reagent—A 1 per cent. solution of 3:3′-dimethylnaphthidine in glacial acetic acid.

Procedure—Add one drop of reagent to one drop of acid VO_3' test solution (1·0 *N* with respect to sulphuric acid) in a depression on a spot tile. In the absence of other oxidising agents a red-violet colour denotes vanadium.

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R. BELCHER
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THE UNIVERSITY
BIRMINGHAM, 15

January, 1951

FORMATION OF SILICOMOLYBDATE

IN the course of an investigation into the colorimetric estimation of silica by means of the reduced molybdenum-blue method, it became necessary to study the formation of silicomolybdate. Previous workers have shown that, although silicomolybdate will only form in weakly acid solution (between limits of pH 1 and pH 5), it is quite stable in a strongly acid medium. This fact permits the estimation of silica in the presence of phosphate. Although phosphomolybdate will form within a wide pH range, it will not reduce to molybdenum blue in a strongly acid solution. Hence, in the presence of 0·1 *N* sulphuric acid, silicomolybdate will form, and if the acidity is then increased to 2 *N* the compound will reduce to give a molybdenum-blue colour. Phosphomolybdate (and arsenomolybdate) will not reduce if the solution is more strongly acid than 1·5 *N* in sulphuric acid.

It is not generally recognised that in dilute solutions silicomolybdate will not form quantitatively unless the solution is heated for some time. For accurate results, therefore, it is essential that the estimation be carried out in two parts, namely—

(*i*) The formation of silicomolybdate by boiling in weakly acid solution.

(*ii*) The reduction to molybdenum blue in strongly acid solution.

Table I indicates the difference between results when silicomolybdate is allowed to form at room temperature, which is the usual procedure, and those when the heating technique is adopted. This work is being reported in full elsewhere.

TABLE I

DEVELOPMENT OF MOLYBDENUM-BLUE COLOUR MEASURED AS THE READING ON A SPEKKER ABSORPTIOMETER

	Coupling conditions					
	15 mins. at 7° C	15 mins. at 15° C	15 mins. at 37° C	15 mins. at 60° C	15 mins at 100° C	24 hours at 7° C
Test solution* ..	0·43	0·51	0·54	0·66	0·90	0·64
Blank without SiO_2	0·07	0·08	0·08	0·09	0·10	0·08

* A solution containing 4 p.p.m. of SiO_2 with 0·4 per cent. of sodium molybdate in 0·1 *N* sulphuric acid, finally made up to 2 *N* in sulphuric acid before development of colour with 0·02 per cent. stannous chloride solution.

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January, 1951

THE COLORIMETRIC DETERMINATION OF METHIONINE

McCARTHY and Sullivan[1] described a colorimetric procedure for estimating methionine, but the authors and others have not found it entirely satisfactory. Recently, Csonka and Denton[2] thoroughly investigated McCarthy and Sullivan's nitroprusside method and, after careful experiments, introduced refinements that made the colorimetric estimation of methionine more practicable and accurate.

We find that the modified method is still not entirely satisfactory, and that Csonka and Denton do not use sufficient hydrochloric acid to bring out the maximum red colour. Much better results are to be had by adding 2 ml of concentrated hydrochloric acid in the final stage of the test.

We also experienced great difficulty during the hydrolysis[1] of the materials, especially with the legumes that we have been investigating. With 2 ml of acid added to 0·5 g of the air-dried powdered materials, the mixtures almost invariably caked and severe bumping and even mild explosions have frequently occurred. Modifications were made and led to trouble-free and excellent results.

METHOD

Hydrolysis—Hydrolyse the materials by gently boiling 1 g of the finely powdered air-dry material with 5 ml of 20 per cent. hydrochloric acid for 24 hours. The hydrolysis stills are provided with several water condensers arranged in series. Instead of heating in an oil-bath,[1] for which no special advantage could be found, it is possible to heat over a small flame that just keeps the mixture gently boiling. Addition of one or two perforated glass beads helps to prevent vigorous bumping. If the mixture cakes, a small addition of 20 per cent. hydrochloric acid is made and the final volume after hydrolysis is reduced by evaporation on a bath of boiling water.

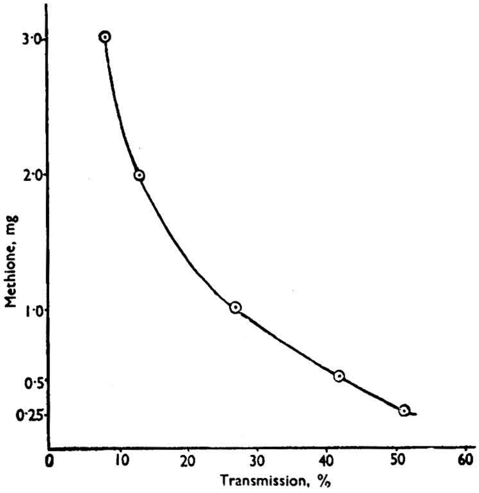

Fig. 1. Standard calibration curve

Precipitation of basic amino-acids—We have found it advisable to use 100 per cent. phosphotungstic acid for precipitating the basic amino-acids. Usually further clarification is not necessary; if it is, decolorisation can be effected with activated carbon. After the second centrifugation from the ice-bath, the clear supernatant fluid is carefully decanted to the last drop and neutralised to the light green colour of bromocresol green (pH 4 to 5) with 5 *N* sodium hydroxide, made up to a known volume (usually 8 to 10 ml) and filtered through a dry filter.

Development of the red colour—Four-millilitre aliquots of the filtrate are taken, 2 ml of 5 *N* sodium hydroxide and 1 ml of 1 per cent. sodium nitroprusside solution are added as in Csonka and Denton's method, the solution is warmed for 8 minutes in a water-bath at 40° C and cooled in an ice-bath for 5 minutes and then 2 ml of pure concentrated hydrochloric acid are added to develop the red colour. Experiments with various volumes of different strengths of hydrochloric acid, pure concentrated hydrochloric acid, syrupy phosphoric acid and hydrochloric - phosphoric acid mixtures have shown that the addition of 2 ml of pure hydrochloric acid brings out the maximum red colour in the final solution.

Calibration curve—A "Lumetron" photo-electric colorimeter with filter No. 530 has been used for preparing the standard calibration curve shown in Fig. 1 and for colour comparisons.

RESULTS

Results of some methionine estimations and recoveries are shown in Table I. The methionine contents of the materials appear to be of the same order as those found by Csonka and Denton and appreciably lower than the values previously reported by Rudra[3] for a modified Baernstein method. Although the Vetch pea (*Lathyrus sativus*) that we have examined is very rich in protein, containing 29 per cent. (other workers, Lewis, Fajans, Esterer, Chao-Wen Shen and Oliphant,[4] have reported a lower protein content), it contains very little methionine when compared with other legumes popular in India; even rice is very much richer in methionine. The relationship of this low methionine content of *Lathyrus sativus* and lathyrism is under investigation, as we believe that methionine deficiency is one of the etiological factors in human lathyrism.

TABLE I

DETERMINATION AND RECOVERY OF METHIONINE

Material	Amount of material in aliquot, g	Methionine					
		Amount in aliquot, mg	Amount in sample, %	Amount added, mg	Amount found,* mg	Recovery of added methionine, mg	Recovery of added methionine, %
Vetch pea (*L. sativus*) ..	0·52	0·31	0·06	—	—	—	—
Moong (*P. radiatus linn*) ..	0·40	1·10	0·28	—	—	—	—
Bengal gram (*C. arietinum*)	0·43	1·08	0·25	—	—	—	—
Red gram (*Cajanus indicus*)	0·20	0·30	0·15	—	—	—	—
Rice (*Oryza sativa*)	0·50	1·06	0·21	—	—	—	—
Lentil (*Lens esculenta*) ..	0·25	0·18	0·07	2·0	2·16	1·98	99
Casein (non-dried)	0·05	0·36	0·72	1·0	1·40	1·04	104

* After addition of extra methionine.

One of us (L. M. C.) is indebted to the Bihar Board of Medical Research for a Junior Research Fellowship that enabled him to take part in this investigation.

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DEPARTMENT OF MEDICAL CHEMISTRY
DARBHANGA MEDICAL COLLEGE
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M. N. RUDRA
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Official Appointments

PUBLIC ANALYST APPOINTMENTS

NOTIFICATION of the following appointments has been received from the Ministry of Food since the last record in *The Analyst* (1951, **76**, 382).

Public Analyst	*Appointments*
CAHILL, Terence John (Deputy)	County of Durham.
LEES, Arnold (Deputy)	City of Lancaster.
WALKER, George Hugh	City of Lancaster.

OFFICIAL AGRICULTURAL APPOINTMENT

NOTIFICATION of the following appointment has been received from the Ministry of Agriculture and Fisheries since the last record in *The Analyst* (1951, **76**, 382).

Agricultural Analyst	*Appointment*
CAHILL, Terence John (Deputy)	County of Durham.

British Standards Institution

NEW SPECIFICATIONS*

B.S. 577 : 1951. Hexachloroethane. Price 2s.
B.S. 579 : 1951. Technical Ether. Price 2s.

DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to interested members of the Society, and may be obtained on application to the Secretary, Miss D. V. Wilson, 7–8, Idol Lane, London, E.C.3.

Draft Specification prepared by Sub-Committee NFE/–/3—Sampling and Analysis of Aluminium and Aluminium Alloys.

CN(NFE) 1295—Draft B.S. for the Determination of Small Amounts of Copper in Aluminium and Aluminium Alloys (Absorptiometric Method).

Draft Specification prepared by Sub-Committee NFE/13/2—Sampling and Analysis of Raw Copper.

CN(NFE) 1813—Draft B.S. for the Determination of Cadmium in Copper-Cadmium Alloys (Electrolytic Method).

International Commission for Uniform Methods of Sugar Analysis†

REPORT OF THE PROCEEDINGS OF THE TENTH SESSION, 1949

THE Tenth Session of the Commission was held at the University of Brussels, Belgium, from August 15th to August 19th, 1949; sixty-three members attended representing fifteen nations. The President was Dr. Frederick Bates, U.S.A., and the Secretary was Dr. F. Tödt, Germany.

The world war of 1939–1945 and its aftermath imposed a gap of thirteen years between the Ninth and Tenth Sessions. Of former members many had died during this period and others were unable to attend the Brussels meeting, but a number of new members enjoyed an International Session of the Commission for the first time. During these years the scientific control of the sugar industry had continued to grow and extend and it was found necessary to place on the agenda 21 subjects for discussion as against 17 at the Ninth Session.

Since previous notice of any changes in the Constitution and By-Laws had not been given, it was agreed that changes, if any, must be referred to the next meeting of the Commission. It was felt by many members that some alternative to the title of the Commission was called for. The wide range of industrial as well as analytical problems that came under review made the present title inadequate. Reports and recommendations on the following subjects were presented.

WEIGHING, TARING, SAMPLING AND CLASSIFICATION OF SUGARS—

Two reports were given, one from the U.S.A. National Committee and one from the British National Committee. The former set out the procedural details for handling raw sugars as received from the Raw Sugar Centrals in bags or by bulk cargo, and also contained a note on the conditions of grain size and the moisture - polarisation relationships for a raw sugar to be classified as a good raw sugar from the viewpoint of the manufacturer and the refiner.

The British Committee's report was in two sections. Section 1 gave a summary of the rules of the Sugar Association of London, supplemented by practice at the refineries. Section 2 indicated a suggested procedure for handling raw sugar in bulk and also made proposals for mechanical mixing of raw sugar samples under appropriate atmospheric conditions.

DETERMINATION OF THE ASH CONTENT OF SUGAR PRODUCTS—

H. C. S. de Whalley (Great Britain) dealt with the conductometric method and the double sulphation method. Some modifications in each method were described and a number of recommendations made, including one to discontinue the 10 per cent. deduction from sulphated ash.

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* Obtainable from the British Standards Institution, Sales Department, 24, Victoria Street, London, S.W.1.

† Printed in England and published by the International Commission for Uniform Methods of Sugar Analysis. Chairman, Publication Committee: Lewis Eynon, 7 and 8 Idol Lane, London, E.C.3. 1950. Price 5s. Issued as a Supplement to *The International Sugar Journal*, June–July, 1950.

Proposals for further work were suggested and the paper included a useful summary of recent literature.

H. E. C. Powers (Great Britain) compared gravimetric with conductivity ash measured at different degrees Brix and graphs are reproduced showing the resistance - Brix relation at different ash contents and the per cent. ash - C ratio.

In the discussion, J. Vernon (Australia) observed that the suggestion to discontinue the 10 per cent. deduction from sulphated ash would affect the basis of payment for raw sugars in Australia, which is based on net rendement.

DETERMINATION OF REDUCING SUGARS—

The report surveyed a number of methods used throughout the sugar industry for the determination of invert sugar in refined sugars, raw beet sugars, beet molasses and cane sugars of low invert content. Ofner's method as modified by Jackson and McDonald gave increased reproducibility and yielded results of the same precision as that of the Berlin Institute method. C. A. Fort had extended the scope of the Lane and Eynon method to include more dilute solutions than those used by the authors. The convenient and rapid routine control method devised by H. C. S. de Whalley was referred to for the determination of invert sugar in refined white sugar. The U.S.A. committee would appreciate any information concerning modifications of the methods referred to in their report. They recommend studies to be made (*a*) comparing the modified Ofner's method with the modified Lane and Eynon's method for small amounts of invert sugar in presence of sucrose and (*b*) on the necessity for defecating specific products, the most suitable defecant and the procedure for removing unused defecant.

L. Eynon and J. H. Lane (Great Britain) presented a very useful note on the preparation of a stable solution of invert sugar the titre of which will remain constant permanently.

STANDARD TESTS FOR THE PERFORMANCE OF BONECHAR AND DECOLORISING CARBONS—

G. P. Meade (U.S.A.) read the report of V. R. Deitz which summarised a survey of the existing test procedures, fifteen of which had been selected for study by the Bonechar Research Project, Inc. An example was given of the proposed investigation on one of the items, "Chemical Analysis for Sulphur in Bonechar."

At the present session the report stated that not even a tentative procedure could be submitted for approval on decolorisation and ash removal tests, but it was anticipated that a report could be reasonably expected at the next meeting. At the Ninth Session (1936), K. Smolenski had made some specific recommendations in the test for decolorising power and Kurt Löwy (Brazil) communicated some pertinent comments on these earlier proposals.

G. W. Payne (Great Britain) examined the standard method for decolorising power adopted at the Ninth Session in special reference to particle size, the importance of which was not previously recognised. This paper also gave details of an improvement in the method of bulk sampling of deliveries of new char.

TESTING OF MOLASSES AND SUGAR SYRUPS—

J. G. Maltby (Great Britain) referred to the Ninth Session recommendations and suggested certain changes under the following heads: (*a*) Replacement of optical by chemical methods for sucrose, (*b*) total sugar as invert sugar, (*c*) Lane and Eynon constant volume method for reducing sugars and (*d*) fermentable and unfermentable sugars.

(*a*) Chemical methods were now used almost exclusively in Great Britain; they obviated some of the sources of error in the Clerget method and offered certain advantages. On average the Clerget method gave rather high results for sucrose. For accuracy, invertase should be used in preference to acid inversion, but for certain types of control the simpler acid inversion was sufficient. (*b*) Although for Customs purposes in Great Britain duty was levied on the sum of the sucrose and reducing sugars, for calculating yields of yeast and alcohol both sugars should be expressed in the same units and one determination by the chemical method of the total sugars, as invert sugar, was all that was required. Normally no clarification was necessary. (*c*) This modification had been in use in the Customs Laboratory for many years but had not been published. Its great advantage was that it dispensed with the Lane and Eynon tables. One method of the constant volume modification was described and others were in use in various laboratories. When sucrose was present a different factor must be applied; factors were given for sucrose ranging from 0 to 12·5 g present in reaction flask. (*d*) These figures would be useful, but no published method was suitable for routine testing. The referee was carrying out an investigation and suggested that this should be a new subject for the next session.

H. C. S. de Whalley gave details of the chemical method of determination of sucrose with invertase solution on behalf of the British National Committee. He also recommended that defecation should be dropped and that treatment with potassium oxalate solution only (to remove lime salts) was sufficient to give a clear end-point and good agreement.

During discussion it was stated that the differences between sucrose by Clerget and sucrose by the chemical method using invertase varied according to the product under examination; for dark coloured materials the random error when using the chemical method is smaller. Jackson and Gillis No. IV method (polarimetric) gives the nearest agreement with the invertase chemical method.

The U.S.A. sub-committee on this subject circulated a detailed summary of recommended methods for (1) Sucrose in Cane Molasses and Syrups, (2) Reducing Sugars in Cane Molasses, (3) Sucrose and Raffinose in Beet Molasses, (4) Reducing Sugars in Beet Molasses and (5) Weight per gallon of Molasses and Syrups. J. Vernon gave a summary of the methods used in this connection by the Colonial Sugar Refining Co. of Sydney.

In discussion, G. P. Meade referred to the differences caused by the various methods of preparation of the solutions. He preferred no lead defecation but de-calcifying with oxalate.

REFRACTIVE INDICES OF SOLUTIONS OF SUCROSE, DEXTROSE, LAEVULOSE, RAFFINOSE, INVERT SUGAR AND MIXTURES—

C. F. Snyder (U.S.A.) reviewed the work on this subject accomplished at previous sessions, notably the Eighth and Ninth. It was considered essential that accurate values on indices of sucrose to five decimal places over the entire range be made available in order to utilise fully the precision of modern refractometers. At present such data exists only up to 24 per cent. of sucrose and further study should be given to the range of 25 to 85 per cent. sucrose solutions.

As regards the refractive indices of solutions of other sugars, the Committee's recommendations as the most accurate values at present available were (*a*) Zerban and Martin for dextrose at 20° C, (*b*) Zerban and Martin for invert sugar at 20° C and (*c*) Jackson and Mathews for laevulose at 20° C as re-calculated by the Saunders equation. Further study was suggested for the refractive indices of raffinose and for the application of refractometric methods to the analysis of mixtures.

H. C. S. de Whalley read a paper on the Refractometric Solids of Sugar Syrups containing Invert Sugar. In the past, corrections on account of invert sugar had been made on the basis of varying degrees Brix and also on the basis of the invert sugar content. It was now proposed that the correction formula for commercially prepared syrups containing reversion products should be $y = 0{\cdot}00025x$, where x equals the true or corrected solids. For low invert contents the observed solids can be used in the formula without serious error.

STANDARDISATION OF QUARTZ CONTROL PLATES—

Dr. E. Einsporn (Germany) contributed a paper which was read by Dr. F. Tödt. Reference was made to the recommendations on this subject at the Eighth and Ninth Sessions. The question now brought forward was the correlation of the attested sugar value, S_{20}, of an international plate valid at 20° C and a sugar value, S_t, such that S_t serves as a control of the International Sugar Scale used at t° C. The following equation had been proposed by the Deutches Amt für Mass und Gewicht, to which the work of the former Reichanstalt in the Eastern Zone of Germany had been transferred—

$$S_t = S_{20}[1 + 0{\cdot}000322\ (t - 20) - 0{\cdot}00000279\ (t - 20)^2]$$

A table based on this equation was presented for the range 7° to 33° C, and a second table of correction factors to be applied to the polarisation of the normal solution of sucrose when the temperature of the solution (t_1) differs from the standard temperature t marked on the brass normal weight, on the flask, and on the normal tube of glass.

It was recommended that the four National Physical Laboratories of the U.S.A., Great Britain, France and Germany should collaborate in an intercomparison of interchanged national sets of control plates for testing the validity of the above proposed equation and the tables based thereon.

SPECIFICATIONS FOR THE EVALUATION OF THE REFINING QUALITIES OF RAW BEET SUGAR—

A report was presented by the Danish Sugar Co. The suitability of raw beet sugar for refining should be considered with regard to the untreated sugar as well as to the affined sugar. For the former, the yield, storage quality, colour and bacteriological tests were recommended. As regards the affined sugar, a standardised treatment was described in some detail for determinations of ash, water, pH and alkalinity, invert sugar, colour, affination, turbidity and size and uniformity of grain.

The tests for size and uniformity of grain as determined by using special sieves were somewhat similar to those published in 1948 by H. E. C. Powers (Great Britain), who gave a report on grist or grain size. His report described the technique of a method whereby the grain size was represented by a numerical index for the M.A. (mean aperture) and uniformity by an index for the C.V. (coefficient of variation). Standard glass plates had been prepared on which synthetic mixtures of sugar of pre-determined M.A. and C.V. have been set in a coating of transparent wax. An adequate series of such plates could supplant the whole gristing tests and, if carefully handled, could be used for an indefinite time. If an unknown sugar was spread similarly upon a glass plate and examined either by the unaided eye or by a binocular magnifier and compared with the standard plates, the correct M.A. and C.V. could be interpolated with surprising accuracy.

METHODS FOR THE EVALUATION OF THE REFINING QUALITIES OF RAW CANE SUGAR—

H. I. Knowles (Canada) stated that among the refining qualities of interest to the refiner and for which methods of evaluation are available, are the following: (1) grist or crystal size, (2) crystal purity, (3) water insoluble matter, (4) filtrability, (5) colour and (6) soluble ash. Each of these was referred to in the report and details of methods proposed for the first three were given very fully. It was recommended that these three methods be subjected to collaborative study and that further work be undertaken to investigate the Bomb Filterleaf for the Elliott filtrability test on the lines described in the report.

The Danish Sugar Company presented a report describing an apparatus they have devised for the direct determination of filtrability. The time in seconds taken to filter, under constant pressure, a pre-determined volume difference is measured and an equation is given relating the coefficient of filtration, FK, with the difference in time taken. A factor, q, which is tabulated, involves the filtering area and the size of the intervals.

SPECIFICATIONS AND TOLERANCES FOR PURE PRODUCTS—

(a) *Sucrose for verifying the saccharimeter scale*—L. Eynon and J. H. Lane (Great Britain) observed that great progress in refinery technique had made it possible to obtain directly sugar that could be safely assumed to have a sucrose content of not less than 99·99 per cent., a degree of purity more than sufficient for standardising the saccharimeter. They recommended the use of this sugar for purposes of standardisation as preferable both as regards purity and convenience to the lengthy purification processes prescribed at the Third Session held in 1900.

A technical note on details of preparation of such highly refined sugar and methods of test was given by H. C. S. de Whalley.

The sub-committee of the U.S.A. National Committee presented a specification for pure sucrose. The pure refinery sugar just referred to was well within the recommended tolerances.

(b) *Basic lead acetate solution and* (c) *dry basic lead acetate*—The U.S.A. sub-committee presented specifications based on the American Chemical Society's specifications for both these reagents. The Australian specification for (*c*) permits a slightly lower limit for the basic lead (PbO) content.

SPECIFICATIONS FOR TESTS FOR THE EVALUATION OF THE CRYSTALLISING QUALITIES OF BEET AND CANE SUGAR FACTORY JUICES—

This subject is one on which no previous recommendations have been made. Two reports were presented, one by the U.S.A. National Committee and one by the Danish Sugar Company; the former suggested study on a method based on the residual purity or concentration of a syrup of predetermined standard concentration that has been treated with a standard quantity of seed and cooled over a prescribed schedule. The effect of viscosity also required close study. Although the preliminary work would be large the comparative simplicity of the whole operation made the method appear attractive. The Danish Sugar Company's report included a mathematical treatment of the methods of de Vries and Kucharenko and deduced an expression relating the rate of crystallisation (K) with the increased weight of the seed crystals. Graphs are given and viscosity curves have been introduced in the graphs. Determination of K using varying sizes of crystals had shown good agreement.

COLORIMETRY, NEPHELOMETRY, REFLECTOMETRY AND FLUORESCENCE IN THE SUGAR INDUSTRY—

O. Wiklund (Sweden) presented a long report that has been published in full elsewhere and made a number of recommendations. These included a statement of units, terms and symbols to be used in colorimetry when results of spectrophotometric absorption measurements on sugar solutions are reported.

H. C. S. de Whalley read a paper on the preparation of solutions for colorimetry. For filtration he stressed the necessity for very high grade kieselguhr that has been previously treated with sulphuric acid to remove fine kieselguhr particles. Neutralisation with soda solution should follow. The absorption of colour by kieselguhr had been over-emphasised. The term "colour" of a sugar solution required definition and he proposed that it should be the absorption at 560 mμ of solution filtered with specially prepared "Dicalite Superaid" under standard conditions.

VALUES OF THE CLERGET DIVISOR AND METHODS FOR MULTIPLE POLARISATION—

The long and valuable report on this subject by the referee (Dr. F. W. Zerban) is ably summarised in the *Proceedings*. Investigatory work done since 1936 (some of it privately communicated to the referee) is dealt with. The most recent values of the divisor for different temperatures of inversion are given and also the re-determined values for the coefficients of concentration and reading temperature. Inversion by acid and by invertase is examined and the effect of salts and other non-sugars on the Clerget divisor is referred to. As regards the determination of sucrose and raffinose in beet products, the referee comments on the two-enzyme method of Paine and Balch and also on the method of Osborn and Zisch, which is based on the observation that the optically active non-sugars become inactive in strongly acid solutions. Twelve recommendations were submitted for appropriate action.

A report by H. C. S. de Whalley and N. Albon was presented. This report gave an account of the detection and estimation of raffinose in raw beet sugars by a method of paper chromatography. The introduction of this technique enabled amounts of raffinose as low as 0·05 per cent. to be detected. The method was under active investigation and development at the time of the Brussels meeting.

DETERMINATION OF DRY SUBSTANCE IN SUGARS AND SUGAR PRODUCTS—

The referee's report contained a critical survey of available methods; these were classified under six groups: (1) density, (2) refractive index, (3) distillation with immiscible solvent, (4) drying at atmospheric pressure, (5) vacuum oven at low temperatures and (6) Karl Fischer titration. The special requirements and merits of each method were reviewed. Special attention was drawn to a recent paper by Iles and Sharman where it was shown that the loss of carbon dioxide that occurs in moisture determination by the reaction between amino-acids and reducing sugars was also dependent on ventilation.

DETERMINATION OF THE HYDROGEN-ION CONCENTRATION OF SUGAR FACTORY PRODUCTS—

The referee (H. E. C. Powers), after reviewing the types of equipment now available for pH determinations and commenting on various electrodes recommended that, for official reports, pH in sugar products shall be accepted as that obtained when using a set equipped with a suitable glass electrode at 20° C (or 28° C) standardised with the National Bureau of Standards buffers 4·005 and 9·20 pH, all products being tested at existing degrees Brix.

As regards correction for temperature, this was not possible since the effect varies with different products. An interim report by D. Gross (Great Britain) covering this subject gave an account of some research work still in progress. Determinations of pH over the temperature range 20° to 80° C had been made on standard buffer solutions and certain cane sugar liquors. The temperature effect on the pH of these solutions and liquors varied from very slight to very marked and the results warranted systematic investigation. The research would not be restricted to 80° C as the upper limit.

C. L. Hinton (Great Britain) read a report on the buffering effect of sugars and described a titration method using 0·1 *N* hydrochloric acid and a stock buffer solution whereby the buffer power of the sugar at pH 4·0 could be rapidly determined.

ANALYSIS AND EVALUATION OF REFINED SUGARS—

The referee (G. P. Meade) remarked that although there was little commercial demand for the chemical testing of refined sugars, there was a growing interest for a standard procedure for evaluating the quality of this product. Primarily tests of physical characteristics were called for, such as colour and turbidity of solution, crystal size, moisture, foaming tests, volume weight and sediment. A number of tentative recommendations were made together with suggestions as to special applicability to refined sugars of tests previously described for the evaluation of the refining qualities of raw beet and raw cane sugar.

A method for the determination of starch in powdered sugar was described and a second report was presented on refined sugar evaluation and analysis by the Danish Sugar Company, dealing with ash, colour, turbidity, "redness" and grain size.

DESIGN AND STANDARDISATION OF LABORATORY APPARATUS—

No report was submitted to the Commission, but a summary of the report of the U.S. National Sub-Committee is included in the *Proceedings*.

DETERMINATION OF VISCOSITY AND SURFACE TENSION OF SUGAR SOLUTIONS—

The report presented on this subject was the approved report of the U.S. National Committee together with some supplementary notes. It contained a review of the literature on the viscosity and surface tension of molasses and sugar solutions and some recommendations on experimental methods. A brief review of the surface tension of solutions of sugars and sugar products by A. Van Hook is also included.

STANDARD METHOD FOR THE DETERMINATION OF ELECTRICAL CONDUCTIVITY OF SUGAR SOLUTIONS—

No report was submitted; it was agreed that the subject should be deleted from the programme.

REDUCTION OF THE LEAD ERROR IN POLARISING RAW SUGARS—

A. H. Rheinlander (Great Britain) referred to the Ninth Session where the British delegation had expressed their disagreement with the recommended use of dry lead for clarification. He presented a report summarising the conclusions reached after a further study on the comparative polarisations of cane raws by the wet and dry methods. Several members of the British National Committee had collaborated in practical work, details of which were set out in the report. It was observed that the British sugar industry was largely concerned with raws polarising about 97° S and at this point the difference between the wet and dry methods was of the same order as the sensitivity of the ordinary laboratory saccharimeter, *i.e.*, ±0·05° S. A number of practical reasons were given for preferring the use of lead solution and the British National Committee concluded (1) that the continued use of the wet method was justified and (2) that the 100° point of the saccharimeter should be divorced from any question of lead defecation.

G. W. Payne in a second paper set out the statistical analysis of a number of polarisations of raw sugars examined by the two methods. The mean difference for British West Indian raws was 0·033° S and for Cuban raws 0·064° S. The average polarisation of both sets of sugars was approximately the same and the effect of the country of origin on the mean difference was observed with interest. The cumulative effect of the small polarisation difference between the two methods would, over a period, have a significant effect on the value of raw sugar cargoes. Attention should be turned to the minimum use of lead and to this end a high level of saccharimeter illumination is perhaps the most important factor.

The discussion that followed these papers was lively and prolonged. The U.S.A. delegation recommended, *inter alia*, the continuance of the dry method as official. If the wet method were used the reading should be corrected by the subtraction of 0·1° S. H. C. S. de Whalley suggested that the correction should be graded. The use of dry lead was supported by a letter from K. Sandera (Czechoslovakia), by J. Vernon (Australia) and by J. Ancizar-Sordo (Columbia). The wet method was favoured by F. W. Hayes (South Africa) and by C. L. Hinton (Great Britain). A. H. Rheinlander opposed a sliding scale of corrections as cumbrous and inexact. Polarisation was an arbitrary figure having no precise scientific meaning, but was commercially of great importance.

A letter was read from K. Löwy (Brazil) advocating clarification with lead solution and de-leading with sodium oxalate before making to volume. A correction was then applied to the polarisation reading dependent upon the volume of lead solution added. The referee commented on this proposal.

The *Proceedings* print full references for all the papers quoted.

The next session of the Commission was fixed for 1953 in Paris.

A. H. RHEINLANDER

Book Reviews

TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS. By I. M. KOLTHOFF and E. B. SANDELL. Pp. xvii + 794. London: Macmillan & Co., Ltd. 1950. Price 30s. net.

This textbook was first published in America in 1936 and was favourably reviewed in *The Analyst* (1937, **62**, 697–698) by S. G. Clarke, who adequately described its character and scope. A revised edition, enlarged by forty-five pages, appeared in 1943 with the subject-matter and its organisation essentially the same as in the first edition. The present volume is merely a reprint of this revised edition and is labelled, pointlessly and unnecessarily, the First English Edition.

As the revised work was not reviewed in *The Analyst*, it is worth while mentioning some of the changes that have been made. A fuller description of organic reagents, eight more well-known reagents being dealt with, and a table showing the empirical formulae of the 8-hydroxyquinoline complexes of the metals, their pH ranges for complete precipitation, and the chief literature references are given. Curiously enough, dithizone is not mentioned in this section, but amends are made in the chapter on Colorimetry and Spectrophotometry, which has been enlarged by nine pages devoted to photo-electric methods. Electro-titrations now include a five-page discussion of amperometric titrations. The chapters on the theory of electro-analysis, on the formation and properties of precipitates and on co-precipitation phenomena have been revised, the section on the ageing and filterability of precipitates being largely re-written. The interesting chapter dealing with Errors in Quantitative Analysis has also been expanded and revised.

The statement that 15° C is the standard temperature in England for the calibration of volumetric glassware (see Clarke, *loc. cit.*) has been removed from the revised edition, but the one (p. 635) that quadrivalent tin is reduced by zinc to the bivalent form has not, unfortunately. Another error that occurs in all three printings of the book is that, in Allen and Bishop's method for determining sulphur in pyrites, the original instructions are that the solution of barium chloride should be added without stirring and not with stirring, as the present authors say.

In their preface, the authors ask for further suggestions to improve this book, and I suggest that, in determining carbon dioxide in limestone (p. 386), they should abandon the use of hydrochloric acid for decomposing the mineral. By using syrupy phosphoric acid instead, they would not only obtain a better attack on the mineral, but they could also simplify the apparatus by using a smaller vessel to contain the sample and by leaving out the unwieldy condenser. The blank for a determination in an apparatus simplified in this way can easily be reduced to about 0·5 mg.

The book is one that can be safely put into a student's hands and any student who wants to learn something of the theoretical background of analytical chemistry will find here much to interest and instruct him.

L. S. THEOBALD

TECHNOLOGY FOR SUGAR REFINERY WORKERS. By OLIVER LYLE. Second Edition. Pp. 525. London: Chapman and Hall Ltd. 1950. Price 32s. net.

Although this is a second and enlarged edition of a book that "was written primarily for the Plaistow Wharf staff," as stated in the author's foreword to the 1941 edition, its appeal is very much wider. The description of sugar refining should be of interest to all who like to know something of the processing of their daily food. For the young technician, be he chemist, physicist or engineer, there is a wealth of well-presented information on a wide range of subjects. The style of writing is lucid and explanations are in the simplest possible words, so that, although it is *not* a "popular science" book, it is as suitable for the general reader as for the trainees for whom it was intended.

The subjects range from an introduction to sugar and the sugar cane, through chapters of general application that give concise pictures of the measurement of physical quantities, an outline of basic chemistry, general methods of analysis, steam generation and use, and electricity, to chapters more specifically pertinent to the sugar industry. This is covered by chapters on special pumps for circulating liquors, vacuum pans, evaporators, methods of filtration and purification. Chapters on the commercial side of the industry, the control and planning of processes, financial balance sheets, the balancing of heat input and work done, the balance between sugar input and output and, more generally, the planning of experiments should be read by all those scientists who have as yet had little experience in the control of industrial processes. The importance of the sugar balance is underlined by the work recently reported in *The Analyst* (**1951**, **76**, **287**) on the effect of the presence of raffinose on the determination of sucrose by the standard methods.

The book itself is well produced. The features include illustrations accompanied by sufficiently full captions to allow them to be understood without reference to the main text; although this means some duplication of matter, extraordinary clarity of exposition has been achieved. The diagrams are clearly drawn.

The author has avoided the more hackneyed illustrations of physical phenomena. Instead of the cohorts of soldiery who march through sand to illustrate the laws of refraction and total internal reflection, Mr. Lyle makes use of a car (pp. 38 and 39), possibly produced by his neighbour at Dagenham.

Apt quotations appear at the head of each chapter and elsewhere; they range from the Tate and Lyle motto from Judges xiv. 14, through Horace ("He seeks to produce not smoke from light but light from smoke") to Shakespeare's "And we must take the current when it serves, Or lose our ventures" (Julius Caesar)—particularly appropriate in times of electrical "load-shedding." Lewis Carroll's classic is represented by the Hatter's remark to Alice about the contents of treacle wells (at the beginning of the chapter on pumps) and by other quotations.

The direct style of the writing, which avoids such "padding" words as "however" and "therefore," is to be commended; it is a matter of regret that sometimes the ordinary laws of syntax have been broken and that sometimes the diction is loose. There is an unhappy sentence on p. 228, where we learn that "The water needed by a jet condenser is given in Table VI."

In the effort to clarify the complicated subject of polarised light, an error has crept into the description of the Nicol prism, p. 77. The author states that light, on entering the prism, "is refracted into two rays, ordinary and polarised," and both text and diagram imply that the former is unpolarised. The Ordinary ray in calcite must, of course, be polarised to the same extent as the Extraordinary ray, although the planes of polarisation are mutually perpendicular. The nomenclature of the rays derives from their behaviour in respect of their refractive indices: the Ordinary ray in calcite has a constant refractive index (ω) of 1·66 for travel in any direction through the crystal, while the refractive index (ϵ) for the Extraordinary ray varies from a minimum of 1·48 to a maximum equal to ω according to the direction the ray travels in relation to the optical axis of the crystal. In the direction of travel in a Nicol prism the particular value of ϵ is 1·534, approximately equal to the refractive index of the Canada balsam cement joining the two halves of the prism. Thus it is purely a matter of convenience that the Extraordinary ray passes through while the Ordinary ray is totally internally reflected and then absorbed in the black wall of the prism container.

The few slips noticed above and about a dozen misprints seen during a careful and highly profitable reading of this book should not affect its value. It is commended to the general and technical reader alike.

J. B. ATTRILL

THE IDENTIFICATION OF MOLECULAR SPECTRA. By R. W. B. PEARCE, D.Sc., F.R.A.S., and A. G. GAYDON, D.Sc. Second Edition. Pp. xi + 276, with 12 Plates. London: Chapman and Hall Ltd. 1950. Price 50s.

The second edition of this book of tables of wavelengths of the bands in molecular spectra brings the original volume, published some ten years ago, up to date.

This work of reference should prove its usefulness in scientific establishments and should be particularly valuable where spectrographic studies are carried out, especially so where the hollow cathode technique is being employed. It should form a companion volume to the M.I.T. tables of Harrison and used in conjunction therewith it should be possible to establish beyond doubt whether nebulous lines are in fact atomic lines or molecular band heads.

The book gives a general table of all persistent band heads in order of wavelength before proceeding to a more detailed treatment of individual systems classified under the particular molecule producing them. Ample references are included for anyone who requires to make a more detailed study.

A short dissertation on practical details of the identification of band spectra and the use of the tables is included, together with a description of various methods that may be used for their excitation.

Finally, for the twelve plates of spectra, the authors deserve special credit. The photographic reproduction of spectra is a matter of some difficulty and is often very indifferently carried out. In this book, not only have these plates been excellently reproduced but in addition they are well annotated, which makes them a really valuable appendix to the tables.

This volume has been clearly printed, well set out and handsomely bound, producing a book of a quality all too rare in publications of this country. It should find a place in all properly equipped scientific libraries. J. A. C. McClelland

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SYSTEMATIC ORGANIC CHEMISTRY. By W. M. CUMMING, I. V. HOPPER and T. S. WHEELER. Fourth Edition. Pp. xxviii + 556. London: Constable and Co. 1950. Price 37s. 6d.

The first edition of this book (1923) aimed at being "more than a collection of recipes" and it was hoped that through it "purely theoretical books would take on a new meaning" for the student. The word "systematic" was used in the title because reaction followed reaction on a definite plan. The sub-title "Modern Methods of Preparation and Estimation" removed any ambiguity as to the scope of the work. The appearance of a fourth edition, revised and enlarged, shows that the book occupies a niche of its own. The price, although very reasonable for a book of this size, is not low for the student's pocket. It is claimed on the dust-jacket that all sections of the book have been modernised and extended "so as to include all the more important developments that have taken place during the last decade."

There is a substantial and well-written new chapter on micro-analysis. The reactions associated with the names of Diels and Alder, Fischer and Tropsch, Hinsberg, Kharasch, Markownikoff, Ponndorf and Zerewitinoff are included, and so also are oxidations with lead tetra-acetate and periodic acid. The Rast method for determining molecular weight is described, but nothing is said about its limitations nor is any alternative mentioned. The Girard reagents do not find a place.

Much progress has been made in recent years in organic chemistry in the field of natural products, in improved isolation procedures and degradations. A systematic treatment of organic chemistry from the point of view of practical techniques ought to place some emphasis on physical methods. Photo-electric colorimetry and ultra-violet and infra-red spectrophotometry are not considered and chromatography gets not quite one page. These techniques together have radically affected many aspects of the quantitative analysis of organic substances.

As a guide to preparative organic chemistry the new edition fully maintains its high reputation, but the revision fails to reflect the movement of new techniques from the periphery to nearer the centre of organic chemistry. R. A. Morton

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ORGANIC REACTIONS. Volumes I to V. Edited by ROGER ADAMS, W. E. BACHMANN, A. H. BLATT, L. F. FIESER, J. R. JOHNSON and H. R. SNYDER. Pp. vii + 391; v + 461; viii + 460; viii + 428; viii + 446. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1942, 1944, 1946, 1948, 1949. Price: 44s., 44s., 48s., 48s., 48s.

This series has now established itself as a compendium that is all but essential to the practising organic chemist. Forty-eight reactions are described from the preparative viewpoint; each chapter deals first with the general nature of the reaction under consideration, then, critically, with its scope and limitations and with typical experimental conditions, including full preparative details for selected products, and finally gives a comprehensive list of examples with full literature citations. Apart from the chapters of obvious analytical interest, *e.g.*, those on periodic acid oxidation (Volume II), the reactions of thiocyanogen (Volume III) and the Diels - Alder reactions (Volumes IV and V), the analyst will find this series of value in two ways; first, for deciding what analogues of known organic reagents are likely to be readily prepared and so worth studying as alternatives to known reagents and, secondly, for devising new methods of organic analysis, since it cannot be doubted that many of the preparative methods so thoroughly surveyed in this series can be made the basis of analytical procedures. H. N. Rydon

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DIE THEORETISCHEN GRUNDLAGEN DER ANALYTISCHEN CHEMIE. By GUNNAR HÄGG. Translated into German by H. BAUMANN. First Edition. Pp. 197. Basle: Birkhäuser AG. 1950. Price 22fr.

A work by Professor Hägg must necessarily command respect and this book will surely capture the admiration of all who read it. The subject-matter is not unfamiliar, but is presented in an eminently refreshing manner. An immense amount of material is dealt with in the space available, and this is accomplished without recourse to misleading simplifications or half truths and without reducing the text to a mere collection of equations, for there are many examples of the applications of the principles laid down.

Naturally, the book is mainly concerned with electrolyte equilibria, but precise and useful chapters are included on adsorption and colloids, and on the properties of precipitates. Bronsted's definition of acids and bases is used throughout, but the less familiar terminology that this involves should present no difficulties. A set of problems (with answers) is provided.

A book of this type has long been needed; for so many books published on quantitative chemical analysis attempt to cover both theory and practice, with the result that the theoretical section is usually quite inadequate. Thanks are due to Dr. Baumann for making this book available to all chemists. The publishers are to be congratulated on a high standard of production.

J. F. HERRINGSHAW

Publications Received

FLOUR MILLING PROCESSES. By J. H. SCOTT, B.Sc. Second Edition. Pp. xvii + 670. London: Chapman & Hall Ltd. 1951. Price 55s.

THE VITAMIN B COMPLEX. By F. A. ROBINSON, M.Sc., Ll.B., F.R.I.C. Pp. xi + 688. London: Chapman & Hall Ltd. 1951. Price 60s.

THE POLAROGRAPHIC METHOD OF ANALYSIS. By OTTO H. MÜLLER. Second Edition. Pp. xii + 209. Easton, Pa. (U.S.A.): Chemical Education Publishing Co. 1951. Price $3.50.

LINEAR POLYMERS. By ELIZABETH M. FRITH and R. F. TUCKETT. Pp. xi + 355. London: Longmans, Green & Co. Ltd. 1951. Price 18s.

BIOLOGY FOR PHARMACEUTICAL STUDENTS AND OTHERS. By S. MANGHAM, M.A., and A. R. HOCKLEY, B.Sc. Second Edition. Pp. viii + 634. London: Baillière, Tindall & Cox. 1951. Price 30s.

HETEROCYCLIC COMPOUNDS. VOLUME II. FIVE- AND SIX-MEMBERED POLYCYCLIC COMPOUNDS CONTAINING ONE O OR S ATOM. Edited by ROBERT C. ELDERFIELD. Pp. vii + 571. New York: John Wiley & Sons Inc. London: Chapman & Hall Ltd. 1951. Price $15.00; 120s.

INTERMEDIATE PRACTICAL CHEMISTRY. By SYLVANUS J. SMITH, M.A. Pp. vii + 248. London: Macmillan & Co. Ltd. 1951. Price 8s.

POISONS. THEIR ISOLATION AND IDENTIFICATION. By F. BAMFORD, B.Sc. Third Edition. Revised by C. P. STEWART, D.Sc., Ph.D. Pp. viii + 316. London: J. & A. Churchill Ltd. 1951. Price 25s.

QUANTITATIVE ORGANIC MICRO-ANALYSIS BASED ON THE METHODS OF FRITZ PREGL. Revised and edited by JULIUS GRANT, M.Sc., Ph.D., F.R.I.C. Fifth English Edition. Pp. ix + 342. London: J. & A. Churchill Ltd. 1951. Price 30s.

PRINCIPLES OF FRUIT PRESERVATION: JAM MAKING, CANNING AND DRYING. By T. N. MORRIS, M.A. Third Edition. Pp. xiii + 206. London: Chapman & Hall Ltd. 1951. Price 21s.

Papers for Publication in THE ANALYST

THE Editor welcomes Papers and Notes for insertion in *The Analyst*, whether from members of the Society or non-members. They are submitted to the Publication Committee, who decide on their suitability for insertion or otherwise.

A copy of the current Notice to Authors, reprinted from *The Analyst*, 1951, **76**, 385, can be obtained on application to the Editor, *The Analyst*, 7–8, Idol Lane, London, E.C.3. All Papers submitted will be expected to conform to the recommendations there laid down and any that do not may be returned for amendment.

THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

FOUNDED 1874. INCORPORATED 1907.

THE objects of the Society are to encourage, assist and extend the knowledge and study of analytical chemistry by holding periodical meetings, by promoting lectures, discussions and conferences, and by the publication of a journal devoted to analytical chemistry; to study questions relating to the adulteration of food, drugs and commercial articles generally, and its detection; and to promote the efficiency and proper administration of the laws concerned with the repression of adulteration.

Every candidate for membership of the Society must be not less than twenty-one years of age and be or have been engaged in analytical, consulting or professional chemistry. Each candidate for election must be proposed by three members of the Society, who must provide written testimony of their personal knowledge of his or her scientific and professional fitness. If the Council of the Society in their discretion think fit, such testimony may be dispensed with for a candidate not residing in the United Kingdom. Every application is placed before the Council and the Council have the power in their absolute discretion to suspend or reject any application, or to elect the candidate to membership.

The Entrance Fee is £1 1s. The Annual Subscription is £2 2s. The Society's official year runs from March to March, but the financial year begins on January 1st and subscriptions are due on that date.

Ordinary Meetings of the Society are held in London, usually on the first Wednesday in October, November, December, February, April and May; the Annual General Meeting is usually held on the first Friday in March. Notices of all meetings are sent to members by post.

The Analyst, the official organ of the Society, is issued monthly to members, and contains reports of the proceedings of the Society, original papers and notes, information about analytical methods, Government reports and reviews of books. All members receive in addition *Abstracts C*, the analytical section of British Abstracts, providing a reliable index to the analytical literature of the world.

Forms of application for membership may be obtained from the Secretary, 7/8, Idol Lane, London, E.C.3.

LOCAL SECTIONS AND SUBJECT GROUPS

THE North of England Section and the Scottish Section were formed to promote the aims and interests of the Society among the members in those areas. Members of the Society residing in England or Wales north of Birmingham may become members of the North of England Section and those resident in Scotland members of the Scottish Section.

The Microchemistry Group, the Physical Methods Group and the Biological Methods Group have been formed within the Society to further the study of the application of microchemical, physical and biological methods of analysis. All members of the Society are eligible for membership of the Groups.

There is no extra subscription for membership of a Section or Group. Application for registration as a member should be made to the Secretary.

The Sections and Groups hold their own meetings from time to time in different places.

MINISTRY OF SUPPLY: PRINCIPAL SCIENTIFIC OFFICER OR SENIOR SCIENTIFIC OFFICER.

THE Civil Service Commissioners invite applications from CHEMISTS for a permanent appointment at the Atomic Energy Research Establishment, Harwell, nr. Didcot, Berks., for work on the electro-magnetic method of separation of stable isotopes. The duties of the post includes:—

(*a*) Supervision of junior staff in the preparation of materials for separation;

(*b*) The establishment of efficient methods of processing separated isotopes to produce them in forms satisfactory for use;

(*c*) Acting as deputy to the project leader with particular responsibilities for the promotion of the use of stable isotopes in physical and radio chemistry.

Candidates must have been born on or before 1st August, 1920, and must possess a 1st or 2nd class honours degree in Chemistry or equivalent qualification and have had considerable relevant experience. The electro-magnetic method of separation is applicable to all polyisotopic elements so that the qualification required for (*a*) and (*b*) above is a wide knowledge of analytical inorganic chemistry.

The Commissioners may, at their discretion, admit a candidate with high professional attainments notwithstanding that he or she may not possess the above qualifications.

Salary scale Principal Scientific Officer (men) £960–£1,295, (women) £840–£1,140, Senior Scientific Officer (men) £720–£910, (women) £595–£810. Post carries benefits under Federated Superannuation System for Universities. Good housing prospects for selected candidate if married.

Further particulars and application forms from the Secretary, Civil Service Commission, Scientific Branch, Trinidad House, Old Burlington Street, W.1, quoting No. S 4045/51.

Completed applications must be returned by 8th August, 1951.

Candidates born between 2nd August, 1920, and 1st August, 1925 (inclusive), may be considered for appointment as Senior Scientific Officer but must apply through the Open Competition under Normal Regulations already announced (No. 3399).

HIS MAJESTY'S COLONIAL SERVICE, MALAYA

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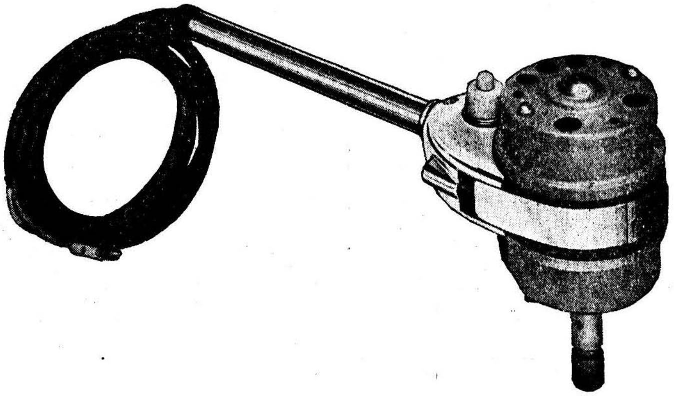

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