

# THE ANALYST

A Monthly Publication  
dealing with all branches  
of Analytical Chemistry:  
the Journal of the Society  
for Analytical Chemistry

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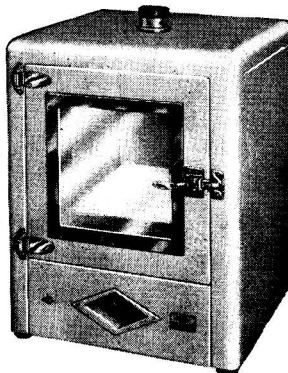
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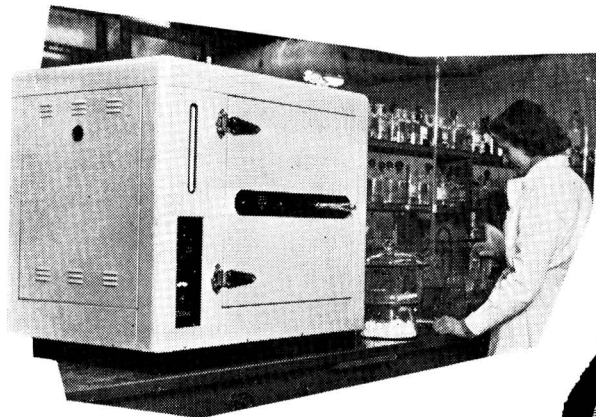
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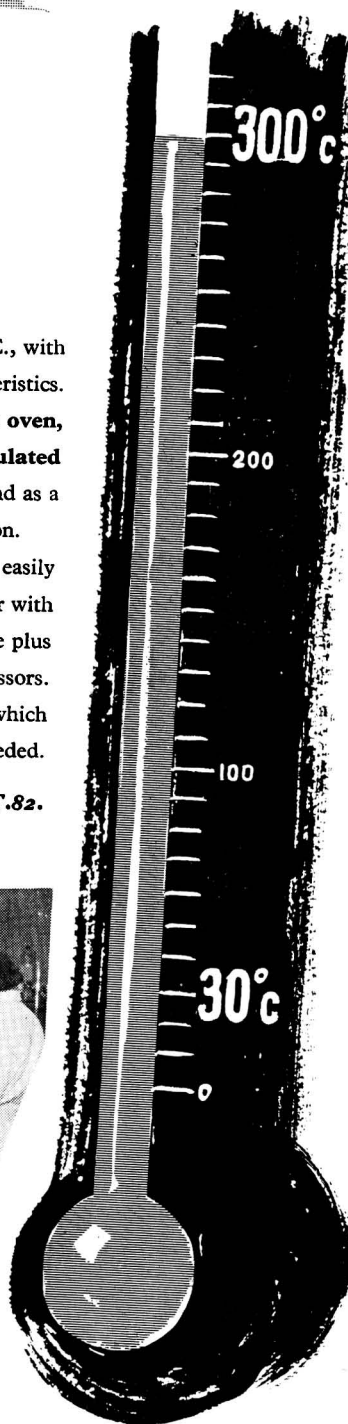
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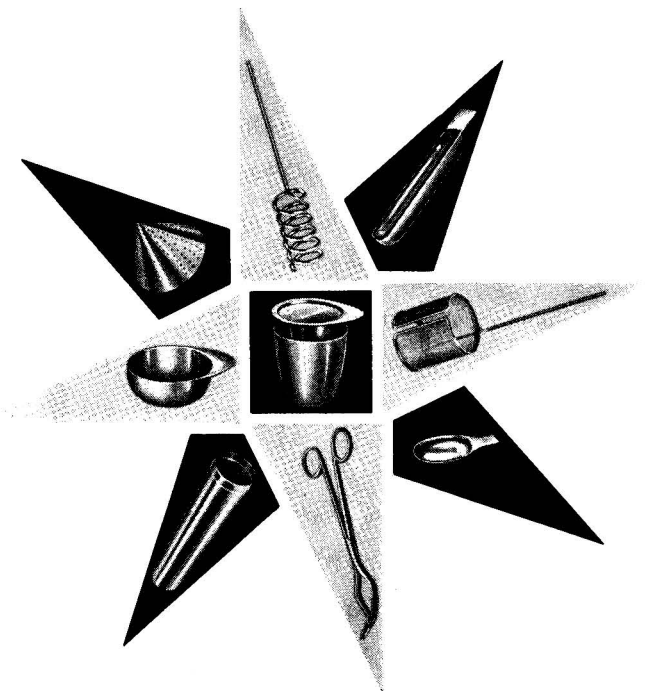


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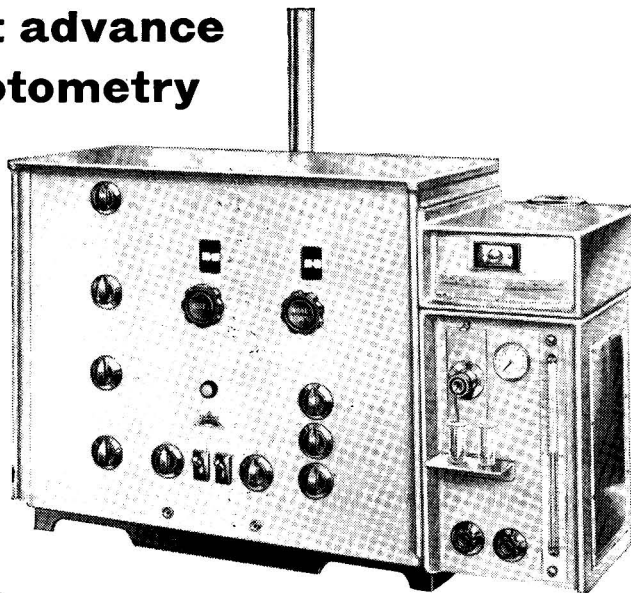
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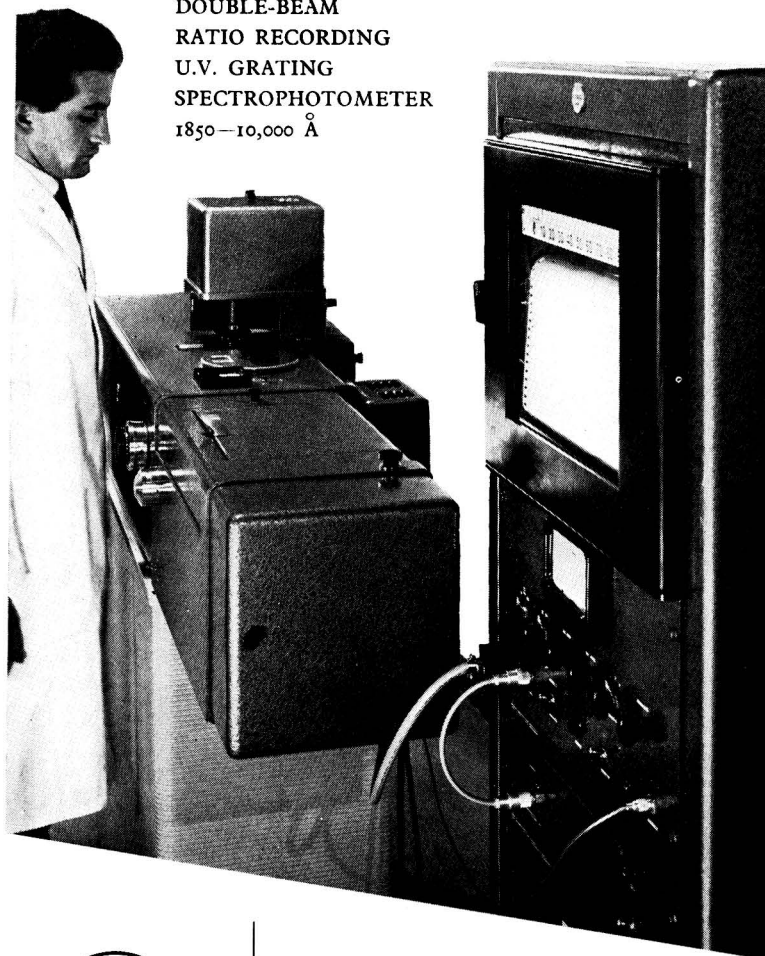
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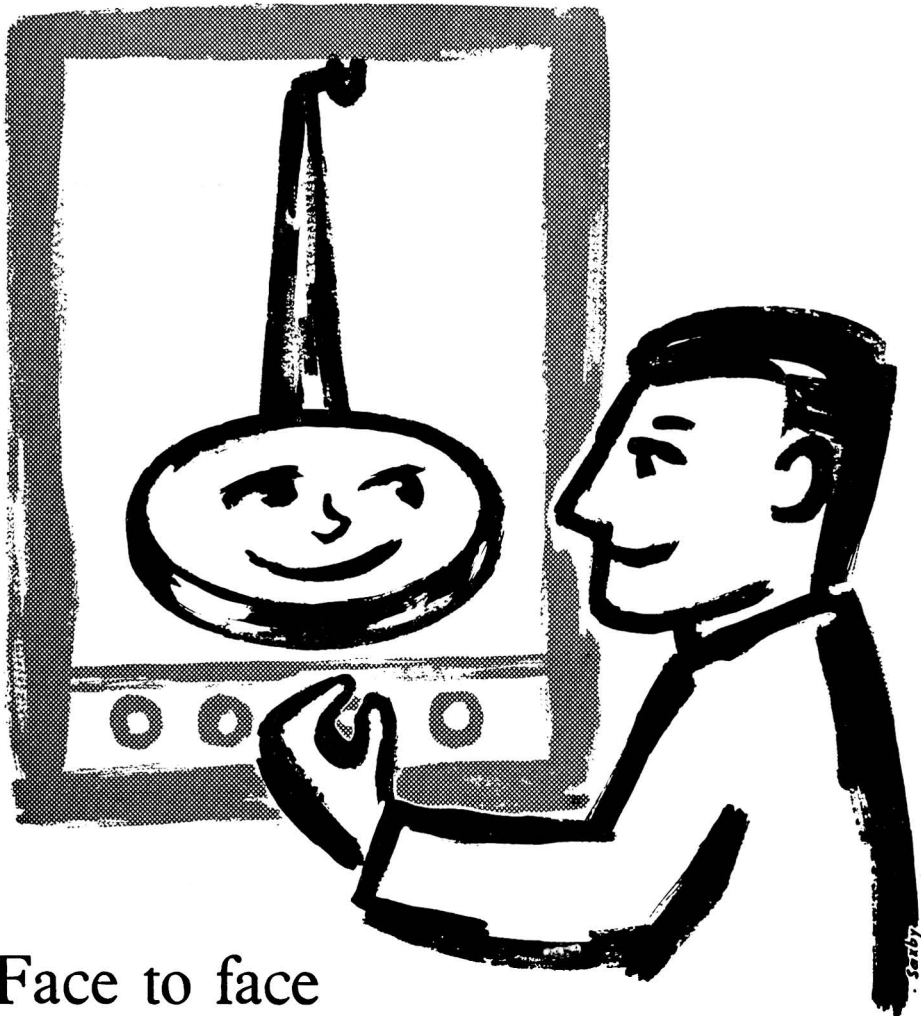
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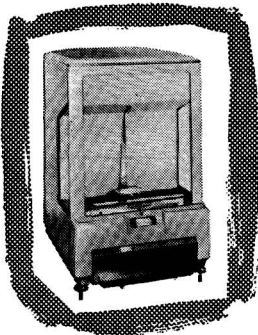
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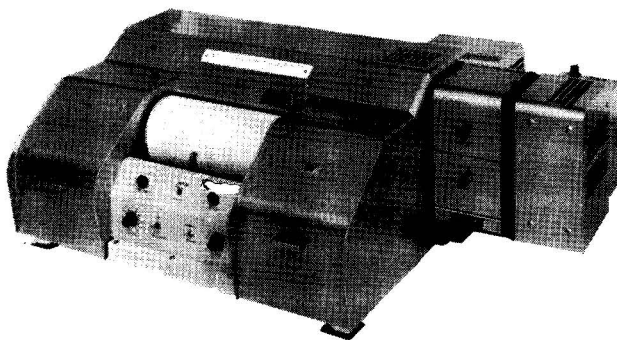
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## PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

### NEW MEMBERS

#### ORDINARY MEMBERS

Derek Abson, B.Sc. (Birm.); Patrick Kieran Hanley, M.Sc. (N.U.I.), H.Dip.Ed.; Clive Holyfield; Charles Abell Horton, A.B. (Cornell), Ph.D. (Michigan); Maurice Jones; David Courtenay Newton, B.Sc. (Lond.); Patrick Noel O'Donoghue, B.Sc. (N.U.I.), A.R.I.C.; Harold Kingsley Packer, M.A., B.Sc. (Oxon.), Dip.Chem.Eng. (Lond.), A.M.I.Chem.E., A.R.I.C., A.M.Inst.F.; Ronald James Starkey, A.R.I.C.; Joseph Martin Stepanek, Dipl.Eng., Dr.T.Sc. (Prague); Leslie Norwood Stuffins, A.R.I.C.; Hubert Morris Thompson, B.Sc., Ph.D. (Liv.), F.R.I.C.; Keihei Ueno, Dr.Eng. (Kyushu); Gerrit Jan Van Kolmeschate, Dr.Phil.Nat. (Utrecht); Arthur Donald Walsh, M.A., Ph.D. (Cantab.), F.R.I.C.; Patricia Olive Whitmore, B.Sc. (Lond.).

#### JUNIOR MEMBERS

James Frederick Marten, A.R.I.C.

#### DEATHS

WE record with regret the deaths of

Julian Levett Baker  
 Alfred Scholes  
 William Henry Woodcock.

#### NORTH OF ENGLAND SECTION

THE thirty-third Annual General Meeting of the Section was held at 2.15 p.m. on Saturday, January 25th, 1958, at the Engineers' Club, Albert Square, Manchester. The Chairman of the Section, Mr. A. N. Leather, B.Sc., F.R.I.C., presided. The following appointments were made for the ensuing year:—*Chairman*—Mr. A. N. Leather. *Vice-Chairman*—Dr. J. R. Edisbury. *Hon. Secretary and Treasurer*—Mr. A. C. Wiggins, J. Lyons & Co. Ltd., 5 Laurel Road, Liverpool, 7. *Members of Committee*—Messrs. A. A. D. Comrie, L. R. Flynn, C. J. House, B. Hulme, A. O. Jones and R. Mallinder. Messrs. F. Dixon and T. W. Lovett were re-appointed Hon. Auditors.

The Annual General Meeting was followed by an Ordinary Meeting of the Section, at which a paper entitled "Micro-organisms in Analytical Chemistry" was given by S. A. Price, B.Sc., F.R.I.C.

#### SCOTTISH SECTION

THE twenty-third Annual General Meeting of the Section was held at 1.30 p.m. on Friday, January 24th, 1958, at the Rhul Restaurant, 123 Sauchiehall Street, Glasgow. The Chairman of the Section, Dr. Magnus Pyke, F.R.I.C., F.R.S.E., presided. The following office bearers were elected for the forthcoming year:—*Chairman*—Dr. Magnus Pyke. *Vice-Chairman*—Mr. A. N. Harrow. *Hon. Secretary and Treasurer*—Mr. J. A. Eggleston, Boots Pure Drug Co. Ltd., Airdrie Works, Airdrie, Lanarkshire. *Members of Committee*—Messrs. D. M. W. Anderson, R. A. Chalmers, R. Kerr, H. C. Moir, J. W. Murfin and A. D. Walsh. Messrs. J. Andrews and J. McL. Malcolm were re-appointed as Hon. Auditors.

The Annual General Meeting was followed by an Ordinary Meeting of the Section, at which a paper entitled "Micro-organisms in Analytical Chemistry" was given by S. A. Price, B.Sc., F.R.I.C.

#### WESTERN SECTION

THE third Annual General Meeting of the Section was held at 12 noon on Saturday, January 11th, 1958, in the Davy House, College of Technology, Ashley Down Road, Bristol. The Chairman of the Section, Mr. P. J. C. Haywood, B.Sc., F.R.I.C., presided. The following appointments were made for the ensuing year:—*Chairman*—Mr. S. Dixon. *Vice-Chairman*—Dr. G. V. James. *Hon. Secretary and Treasurer*—Dr. T. G. Morris, Brockleigh, Clevedon Avenue, Sully, Glamorgan. *Members of Committee*—Messrs. R. G. H. B. Boddy, R. C. Curtis, P. J. C. Haywood, C. H. Manley, J. A. Pickard and G. F. Price. Mr. R. E. Coulson and Dr. Z. Hybs were re-appointed as Hon. Auditors.

The Annual General Meeting was followed by an Ordinary Meeting of the Section, which took the form of a discussion on "Perpetuation of Errors in Text Books."

#### MIDLANDS SECTION

AN Ordinary Meeting of the Section was held at 6.30 p.m. on Thursday, February 13th, 1958, in the Mason Theatre, The University, Edmund Street, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.R.I.C., F.Inst.F.

The following paper was presented and discussed: "Nuclear Magnetic Resonance," by D. H. Whiffen, D.Phil.

## The Spectrophotometric Determination of Nickel in Copper-Nickel Alloys

BY G. R. SUTCLIFFE AND D. M. PEAKE

(Research Department, Imperial Chemical Industries Ltd., Metals Division, Kynoch Works, Witton, Birmingham)

From a study of the absorptiometric characteristics of solutions of copper and nickel, a method has been developed for the direct determination of nickel in copper-base alloys.

The optical density of the sample solution in a nitric acid-phosphoric acid medium is measured at 3950 Å, where absorption is due almost entirely to nickel. A similar measurement is made on the same solution at 4900 Å, where neither copper nor nickel absorb, and this permits a background correction to be made.

The method has been satisfactorily applied to typical copper-base alloys with nickel contents ranging from about 1.5 to 30 per cent. and a single determination can be completed in about 30 minutes, as opposed to 3 hours by a reliable gravimetric procedure.

**DETERMINATION** of alloying amounts of nickel is usually based on the use of dimethylglyoxime.<sup>1</sup> This gravimetric procedure is relatively straightforward and can be applied in the presence of small amounts of copper, but becomes increasingly difficult to apply when a large amount of this metal is present. In such instances, copper in solution can be reduced to the cuprous state,<sup>2</sup> but the most satisfactory way of overcoming this interference is to remove the metal by electro-deposition. A further disadvantage associated with the dimethylglyoxime method, particularly in control laboratories, is the relatively small sample that must be used for the examination of alloys containing 15 per cent. or more of nickel.

#### EXPERIMENTAL

A study of the absorption characteristics of simple solutions of metals was carried out with the idea of developing rapid photometric procedures for the determination of constituents that are commonly present in copper-base alloys containing up to about 30 per cent. of nickel. Absorption characteristics of copper as sulphate, nitrate and perchlorate in corresponding

acid solutions were determined and were shown to be substantially independent of acid concentration (see Fig. 1, curve A).

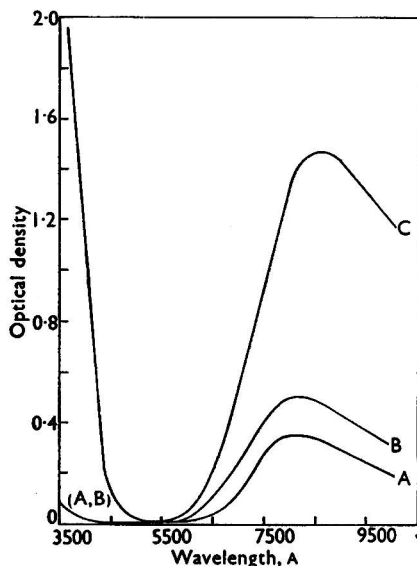


Fig. 1. Absorption spectra of solutions containing 0.2 g of copper per 100 ml: curve A, copper nitrate, sulphate and perchlorate; curve B, copper chloride in 5 per cent. v/v hydrochloric acid; curve C, copper chloride in 30 per cent. v/v hydrochloric acid

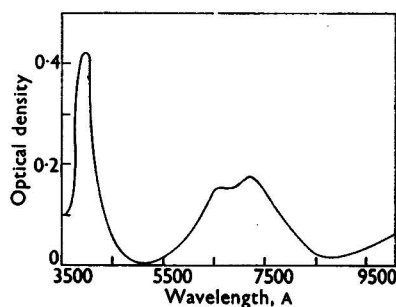


Fig. 2. Absorption spectrum of nickel nitrate, sulphate and perchlorate solutions containing 0.5 g of nickel per 100 ml

Absorption by solutions containing copper chloride and free hydrochloric acid is very largely influenced by acidity; this is attributed to complex-ion formation.<sup>3</sup> An intense absorption by copper chloride solutions occurs at 4000 Å (see Fig. 1, curve C) and the optical density is related to acid concentration. Examination of the absorption characteristics of solutions of copper in hydrochloric acid show that it is undesirable to use this acid in photometric determinations involving absorption at about 4000 Å or between 6000 and 10,000 Å.

Absorption characteristics of nickel as sulphate, nitrate and perchlorate in corresponding acid solutions (see Fig. 2), are substantially independent of acidity.

By comparing curve A, Fig. 1, with Fig. 2, it is interesting to observe that nickel solutions absorb strongly at 3950 Å, whereas copper solutions have no absorption at this wavelength.

Absorption characteristics of iron solutions show that they absorb to some extent at 3950 Å, although nitrate solutions of the metal absorb considerably less at this wavelength than either the corresponding sulphate or perchlorate solutions. It was shown that phosphoric acid represses the absorption due to iron without affecting the absorption characteristics of either copper or nickel. Hence, the optical density due to 10 mg of iron, *i.e.*, 1 per cent. of iron in a 1-g sample, was only 0.001, and it appeared likely that a single optical-density determination at 3950 Å of a simple solution containing both nickel and copper could form the basis of a rapid method for the direct absorptiometric determination of nickel.

Copper and nickel alloys are readily soluble in nitric acid, and curve A, Fig. 1, and Fig. 2 show that this acid is permissible as a solvent. Further, the presence of phosphoric acid prevents precipitation of tin, which is present in some commercial alloys, and a mixed solvent of nitric and phosphoric acids was therefore used.

Solutions containing known amounts of copper and nickel were prepared and these showed good proportionality between optical density and nickel content, although the reproducibility of optical-density measurements was not entirely satisfactory. This was attributed to haze and cell-surface variations, but the difficulty was resolved when it was found that neither copper nor nickel absorbs significantly at 4900 Å. At this wavelength the optical density therefore gives an approximate assessment of the haze and cell blank, and, by measuring the optical

density of the solution at 3950 Å and deducting the value of the optical density measured at 4900 Å, good reproducibility and proportionality were found. When, however, attempts were made to apply this principle to the analysis of alloys containing a small amount of manganese, an unexpected oxidation to permanganate occurred when the sample solution was digested with the phosphoric acid - nitric acid mixture. This reaction is not quantitative and is probably due to oxidation by a perphosphoric acid. Addition of hydrogen peroxide, after dilution, is sufficient to reduce the permanganate and eliminate this interference, and excess of peroxide can be readily decomposed by boiling.

A Unicam SP600 spectrophotometer was used for all optical-density measurements, and as the density scale is logarithmic, the lower end of the scale up to 0.25 was used, which permits accurate readings to be made to within  $\pm 0.001$ . When 4-cm cells are used, this length of scale is equivalent to about 60 mg of nickel, *i.e.*, 6 per cent. of nickel in a 1-g sample. For larger amounts of nickel, say up to 30 per cent., the determination was made by difference, use being made of a reference liquid containing a solution of known nickel content.

These general principles were embodied in a provisional method that was applied to a series of commercial alloys. Nickel in these alloys was also determined by a gravimetric dimethylglyoxime procedure, after preliminary electro-deposition of copper. Two sets of results are shown in Table I. Hence, by dissolution of the sample in a nitric acid - phosphoric acid mixture, dilution to a standard volume and subsequent measurement of the optical densities at 3950 and 4900 Å against a solution containing either copper, or copper and a known concentration of nickel, a rapid and accurate determination of nickel can be made in about 30 minutes once the calibration graphs have been prepared, as opposed to 3 hours by a reliable gravimetric procedure.

TABLE I  
COMPARISON OF RESULTS BY DIFFERENT METHODS

Typical manganese content, %	Typical iron content, %	Nickel found by gravimetric method		Nickel found by proposed method	
		Analyst A, %	Analyst B, %	Analyst A, %	Analyst B, %
0.25	0.05	1.69	1.75	1.70	1.72
		1.89	1.84	1.95	1.98
		2.21	2.18	2.17	2.13
1.2	3.7	4.29	4.37	4.43	4.43
		4.62	—	4.66	4.66
		5.02	—	5.01	—
0.1	<0.05	7.27	—	7.32	7.36
		7.07	—	6.92	6.89
		6.72	—	6.73	6.70
0.2	0.05	6.58	—	6.64	6.61
		9.39	9.46	9.38	9.33
		9.82	9.74	9.71	9.68
0.1	—	9.95	10.03	9.99	9.96
		18.51	—	18.40	18.37
		24.98	—	25.03	25.05
0.15	<0.05	30.34	—	30.22	30.20
		30.26	—	30.25	30.20
		30.37	—	30.32	30.42
1.4	2.2	30.05	—	30.03	30.13
		—	—	—	—

#### METHOD

##### APPARATUS—

A Unicam SP600 spectrophotometer was used.

Grade A calibrated flasks must be used throughout, and, for work of the highest accuracy, the certified volumes must be used in the calculation of the nickel contents.

The cells used for the preparation of the calibration graph must also be used in determining nickel in the test solution.

##### REAGENTS—

Distilled water should be used for the preparation of all solutions.

Nickel—Hilger H.P. quality was used.



*Copper*—The metal nominally free from nickel was used.

*Nitric acid, diluted (1 + 1)*—Dilute 1 volume of nitric acid, sp.gr. 1.42, with 1 volume of water.

*Phosphoric acid, sp.gr. 1.75.*

*Hydrogen peroxide, 2-volume*—Dilute 10 ml of 20-volume hydrogen peroxide with 90 ml of water.

*Standard nickel reference solutions*—Reference solutions contain a combined weight of 1 g of nickel plus copper per 100 ml. The ratio of nickel to copper used for a particular solution is governed by the range of nickel contents to be determined, *e.g.*, a reference solution for nickel in the range 5 to 11 per cent. should contain 0.0500 g of nickel plus 0.9500 g of copper per 100 ml.

Transfer the calculated weight of nickel and copper to make 1 litre of solution to a large beaker. Dissolve it in 100 ml of diluted nitric acid (1 + 1) and add 300 ml of phosphoric acid. Evaporate to ensure removal of all nitrous fumes; it is not necessary to remove all the nitric acid by evaporation. Dilute to about 800 ml, add 20 ml of 2-volume hydrogen peroxide and boil for 5 minutes. Cool, transfer the solution to a 1-litre calibrated flask, dilute almost to the mark and place in a thermostatically controlled water bath at 20° C for 1 hour. Dilute to the calibration mark and mix well.

#### PROCEDURE FOR PREPARING A CALIBRATION GRAPH FOR BETWEEN 5 AND 11 PER CENT. OF NICKEL—

Weigh accurately about 0.06, 0.07, 0.08, 0.09, 0.10 and 0.11-g portions of nickel and to each add copper to make a total sample weight of 1 g. Dissolve the samples in 10 ml of diluted nitric acid (1 + 1), add 30 ml of phosphoric acid and evaporate to small volume to ensure removal of nitrous fumes. Cool, dilute to a volume of about 85 ml, add 2 ml of 2-volume hydrogen peroxide and boil gently for 5 minutes. Cool, transfer to a 100-ml calibrated flask and dilute to the mark at 20° C. Measure the optical density of each solution in a 4-cm cell at 3950 and at 4900 Å with respect to the 5 per cent. reference solution, and record the difference in optical density.

(For other ranges of nickel contents, the procedure is similar and measurements are made by using a reference solution appropriate to the range.)

#### PROCEDURE FOR DETERMINING NICKEL—

Weigh 1 g of sample and continue exactly as described for preparation of the calibration graph. Measure the optical density with respect to the appropriate reference solution and calculate the nickel content from the calibration graph.

Acknowledgment is made to Mr. W. T. Elwell, Division Chief Analyst, Imperial Chemical Industries Limited, Metals Division, for his interest in this investigation and for assistance in the preparation of this paper.

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ห้องสมุด กรมวิทยาศาสตร์

## Volumetric Determination of Uranium in Presence of Iron

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A volumetric method is described for the determination of uranium in presence of iron. It is based on the oxidation of reduced uranium<sup>IV</sup> with ferric sulphate and titration of the excess of ferric iron iodimetrically. Osmium tetroxide has been found to be a suitable catalyst for the reaction.

EXTRACTION of uranium from its ores gives rise to the need for a rapid and fairly accurate method of determining it in solutions containing iron and sometimes also phosphate. A volumetric method that does not involve prior separation of uranium would obviously be rapid and suitable for the routine analysis of a large number of samples. The general volumetric methods of determining uranium are discussed by Rodden and Warf,<sup>1</sup> but all are applicable only in the absence of iron.

The potentiometric titration of uranium<sup>IV</sup> with ferric sulphate as an oxidant has been studied by several workers.<sup>2,3</sup> This method has the advantage that it can be used in presence of iron, but the titration should be carried out at about 90° C by a potentiometric or amperometric method, precautions being taken to exclude air from the titration assembly. This makes it rather unsuitable as a quick and routine method.

It has been observed that at room temperature uranium<sup>IV</sup> can be readily oxidised by addition of an excess of ferric sulphate. The proposed method involves the addition of a known volume of a standard solution of ferric sulphate to the reduced uranium solution and then titration of the excess by the iodimetric method first proposed by Mohr,<sup>4</sup> which consists in the addition of potassium iodide and titration of the liberated iodine with sodium thiosulphate.

### EXPERIMENTAL

#### IODIMETRIC DETERMINATION OF IRON—

Although apparently simple, the accuracy of the iodimetric determination of ferric iron is influenced by several factors. After the original work of Mohr, several workers studied this method in detail,<sup>5,6,7,8</sup> and contradictory statements about the necessary conditions for accurate determination are not rare in the literature. Swift<sup>5</sup> has given an excellent review of these methods. A difficulty in the titration is the reappearance of the blue starch-iodide colour despite its repeated discharge with sodium thiosulphate. This is often referred to as the "oxygen error."

It has been observed<sup>8</sup> in actual titrations that the time required for the quantitative liberation of iodine and the maintenance of the potassium iodide concentration are to a large extent dependent on the concentration of iron<sup>III</sup> and the acid present. It was therefore not possible to adapt, from published work, a set of conditions for carrying out the iodimetric determination of the excess of iron<sup>III</sup> remaining after the oxidation of uranium<sup>IV</sup>. An attempt was made to determine the necessary conditions for a successful determination under the experimental conditions.

The samples contained 50 to 200 mg of U<sub>3</sub>O<sub>8</sub> and various amounts of iron in sulphate solutions. After passage through a Jones's reductor to reduce the uranium and washing the reductor, the volume of the solution was about 150 ml, and it was approximately 2 N in sulphuric acid. Excess of ferric sulphate was added to oxidise uranium<sup>IV</sup>, the excess being 5 to 10 mg of iron.

It was found in a number of experiments that the amount of potassium iodide to be added to this final solution for the quantitative liberation of iodine in a reasonable time (say 5 minutes) was quite high (about 20 g), probably owing to the low concentration of iron<sup>III</sup>. When the sample solution contained an appreciable amount of phosphate, even this amount of potassium iodide was insufficient, since the effective concentration of iron<sup>III</sup> was further reduced by the formation of complexes. In such tests the titre was low and the end-point was not sharp. Similar trouble was noticed when the samples contained a large amount of iron and the concentration of ferrous iron in the final solution was high. This was

because of the reversible nature of the reaction. Whenever a long time was allowed for the liberation of iodine, it was found that the titres were not reproducible and tended to be high, because of the "oxygen error." Studies were therefore undertaken to find a suitable catalyst that would increase the speed of the reaction considerably, thereby permitting the titration to be completed within a short time. This would also reduce the "oxygen error."

Cuprous iodide<sup>9</sup> has been recommended as a catalyst, but even its presence did not help appreciably. After a number of experiments, it was found that osmium tetroxide, in small concentration, was a good catalyst. It was possible to start the titration immediately after the addition of iodide, and the end-point was stable. However, a correction had to be applied to the titre, since osmium tetroxide oxidises iodide to liberate iodine. The correction factor was found by carrying out a blank determination. The method was first tested for the determination of ferric iron and then applied to the indirect determination of uranium in the presence of iron and phosphate.

#### METHOD

##### REAGENTS—

All reagents should be of recognised analytical grade.

*Uranyl sulphate solution*—Dissolve about 15 g of uranyl sulphate in distilled water and dilute to 2 litres. Standardise the solution by precipitating uranium with ammonium hydroxide and igniting to the oxide,  $U_3O_8$ .

*Ammonium ferric sulphate solution*—Prepare an approximately 0.05 *N* solution in 5 per cent. v/v sulphuric acid. Standardise by titration with potassium dichromate.

*Sodium thiosulphate solution*—Prepare an approximately 0.05 *N* solution and standardise iodimetrically against standard potassium dichromate.<sup>10</sup>

*Osmium tetroxide solution*—Dissolve 250 mg of osmium tetroxide in 100 ml of 5 per cent. v/v sulphuric acid.

##### PROCEDURE—

*Determination of iron*—With a pipette place a known volume of ammonium ferric sulphate solution in a 400-ml conical flask and dilute to about 150 ml with 5 per cent. v/v sulphuric acid. Add about 1 g of sodium carbonate with stirring and then stopper the flask loosely. Allow the carbonate to dissolve and then add 10 g of solid potassium iodide and 2 drops of the osmium tetroxide solution, stopper the flask and swirl the contents to dissolve the iodide. Titrate the liberated iodine with sodium thiosulphate solution, using starch as the indicator.

TABLE I

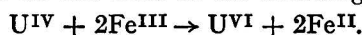
IODIMETRIC DETERMINATION OF IRON<sup>III</sup>

Test No.	Concentration of ammonium ferric sulphate, <i>N</i>	Amount of ammonium ferric sulphate taken, ml	Amount of phosphate added, as $P_2O_5$ , mg	Concentration of sodium thiosulphate used, <i>N</i>	Amount of sodium thiosulphate used,* ml	Calculated amount of sodium thiosulphate used, ml
1	0.0508	10	—	0.0551	9.26	9.22
2	0.0508	10	—	0.0551	9.30	9.22
3	0.0508	10	—	0.0551	9.25	9.22
4	0.0508	10	—	0.0551	9.23	9.22
5	0.0508	20	—	0.0551	18.44	18.44
6	0.0508	20	—	0.0488	20.82	20.82
7	0.0508	20	—	0.0488	20.83	20.82
8	0.0508	20	—	0.0488	20.85	20.82
9	0.0381	20	100	0.0514	14.85	14.82
10	0.0381	20	250	0.0514	14.86	14.82
11	0.0381	20	500	0.0514	14.82	14.82
12	0.0381	20	500	0.0514	14.82	14.82

\* Corrected for a blank value of 0.15 ml of 0.05 *N* sodium thiosulphate for each 2 drops of osmium tetroxide solution added.

*Determination of uranium*—Add 2.5 ml of concentrated sulphuric acid to the solution of uranium sulphate containing about 100 mg of  $U_3O_8$  and dilute to 50 ml. Cool the solution and pass it through a Jones's reductor and then rinse the reductor four times with 25-ml

portions of 5 per cent. w/v sulphuric acid. Bubble clean air through the reduced solution for 5 minutes to oxidise any uranium<sup>III</sup> formed. Add, from a burette, a known volume of ammonium ferric sulphate solution, set the solution aside for 5 minutes and then determine the excess of iron<sup>III</sup> iodimetrically as before. From the amount of ferric iron consumed, calculate the uranium present on the basis of the following reaction—



### RESULTS

Results of the iodimetric determination of iron<sup>III</sup> are shown in Table I. Since phosphate was likely to be present in the sample solutions, its effect on the determination of ferric iron was investigated in tests 9 to 12 (see Table I). The results show that the addition of phosphate equivalent to up to 500 mg of phosphorus pentoxide has no effect on the titration.

Some results for the determination of uranium by the proposed method are shown in Table II.

TABLE II

#### DETERMINATION OF URANIUM BY THE PROPOSED METHOD

Uranium taken, as U <sub>3</sub> O <sub>8</sub> , mg	Iron added, mg	Phosphate added, as P <sub>2</sub> O <sub>5</sub> , mg	Uranium found, as U <sub>3</sub> O <sub>8</sub> , mg
70.0	—	—	70.2
140.0	—	—	139.8
140.0	—	—	140.0
70.0	100	—	70.1
70.0	200	—	70.0
70.0	500	—	70.4
140.0	100	—	139.4
140.0	200	—	140.4
140.0	500	—	141.0
70.0	200	200	69.8
70.0	250	400	70.3
140.0	200	500	140.6

### DISCUSSION

The results shown in Table II indicate that the proposed method is applicable to the accurate determination of uranium in presence of iron and phosphate. The success of the method depends to a large extent upon the accuracy with which the iodimetric determination of ferric iron is carried out. The use of osmium tetroxide as a catalyst in this titration was found to give quite reliable results. Since it is a costly reagent, attempts were made to use some of the more readily available reagents, such as oxalic acid, sodium molybdate and cuprous iodide, but, under the conditions described, they were not satisfactory.

Although the acid concentration of the solutions for titration was adjusted in all these experiments to about 2 *N*, it was found in many experiments that variation from 0.5 to 5 *N* had no appreciable effect on the titration, except when the samples contained phosphate; an acid concentration below 2 *N* would then cause precipitation of uranous phosphate and lead to erratic results.

TABLE III

#### DETERMINATION OF URANIUM IN PRESENCE OF NITRATE

Uranium taken, as U <sub>3</sub> O <sub>8</sub> , mg	Sodium nitrate added, as NO <sub>3</sub> <sup>-</sup> , mg	Uranium found by titration with KMnO <sub>4</sub> , as U <sub>3</sub> O <sub>8</sub> , mg	Uranium found by proposed method, as U <sub>3</sub> O <sub>8</sub> , mg
70.0	0	70.3	69.8
70.0	50	—	69.9
70.0	100	—	70.3
70.0	200	134.2	69.7
70.0	500	—	70.2

Apart from permitting the determination of uranium in the presence of iron, the proposed method has another advantage. In the other volumetric procedures for uranium, in which strong oxidising agents such as potassium permanganate, potassium dichromate and ceric

sulphate are used, nitrate, if present, must be removed by repeatedly heating to fumes with sulphuric acid,<sup>11</sup> otherwise the titres are higher than expected and the end-points are not sharp. Ferric sulphate, being a mild oxidising agent, does not react with the reduction products of nitrate formed during the reduction of a solution of uranium containing nitrate. Hence, by this method, the determination of uranium can be carried out even in the presence of appreciable amounts of nitrate. The results shown in Table III were found for pure solutions of uranium to which nitrate had been added in different amounts before passage through a Jones's reductor. It is clear that the presence of nitrate does not interfere with this titration.

We thank Dr. Jagdish Shankar, Chemist, Atomic Energy Establishment, for his keen interest in the progress of the work.

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## A Spectrochemical Solution Method for the Determination of Copper, Cobalt and Iron in Copper and Cobalt Concentrates

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A solution method of spectrochemical analysis is described, whereby it is possible to determine copper, cobalt and iron in copper and cobalt concentrates over the range 5.0 to 40.0 per cent. for copper and iron, and 0.2 to 6.0 per cent. for cobalt. Excitation is by condensed spark and use is made of the Feldman porous-cup technique. Results show good agreement with chemical analyses, but reproducibility varies, according to the element and its concentration, from 1.25 to 8 per cent. of the amount determined. The time for one analysis is 1 hour, and twenty samples can be analysed in a working day.

IN recent years, details have been published of several successful applications of the spectrographic technique to the determination of major constituents in minerals, ores, slags and ceramics, and ferrous and non-ferrous alloys. In view of these successes, it was felt that the application of such a technique to the determination of copper, cobalt and iron in copper and cobalt concentrates would be desirable.

In the analysis of powdered samples, some workers<sup>1,2,3</sup> have excited the powder directly without any pre-treatment except the addition of buffers such as ammonium chloride and lithium carbonate. The reproducibility of the results by these methods is rarely better than  $\pm 5$  per cent. of the amount present, although errors can arise from the very small amount of sample used (usually  $< 0.1$  g).

Experience has shown that the solution technique<sup>4,5,6</sup> will provide a reproducibility better than  $\pm 3$  per cent. of the amount present. Further, by suitable chemical treatment, it is often possible to prepare a rather complex sample in the form of a relatively simple

solution. Such a transformation would be definitely advantageous when dealing with concentrates containing approximately 20 per cent. of sulphur and silica. In view of these advantages, it was felt that the extra time involved by chemical preparation of the sample would be amply justified.

#### EXPERIMENTAL

##### DECOMPOSITION OF CONCENTRATES—

The object of the decomposition of the concentrates was to remove the silica and sulphur generally present in the sample. Here it was possible to draw on years of experience in chemical assaying of both copper and cobalt concentrates.

Unfortunately, the accepted efficient method of decomposition—attack by a mixture of perchloric, nitric and sulphuric acids—could not be used, as the end-product is a sulphate solution and the spectral emission from such a solution was too weak for further consideration. The methods tried, but which failed to extract all the copper, cobalt and iron, were as follows—

- (i) attack with aqua regia,
- (ii) attack with bromine and aqua regia, and
- (iii) attack with bromine and nitric, hydrochloric and perchloric acids.

*Method of decomposition finally adopted*—A completely efficient and reasonably rapid extraction is achieved by decomposing a 0.5-g sample with bromine and nitric, hydrochloric, hydrofluoric and perchloric acids, the solution being evaporated to a paste, which is then dissolved in hydrochloric acid and diluted to the working volume with water. In this way the sulphur and silica are almost completely removed, the amount of residue being so small (<0.001 g) that filtration is eliminated by allowing the residue to settle before the required aliquot is removed by means of a pipette.

A number of residues, after ignition, were excited spectrographically by using a 7-ampere d.c. arc. Examination of the resulting spectra revealed only a faint trace of copper and iron (<0.001 per cent.), and cobalt was not detected.

##### SOLUTION FOR ANALYSIS—

It was found that spectra of suitable density could be obtained from a solution prepared by adding 5 ml of the sample solution to 1 ml of a standard solution of nickel containing 0.05 g of nickel per ml.

*Method of excitation*—Previous experience with the Feldman porous cup<sup>7</sup> had shown it to be a most satisfactory medium for reproducible excitation of solutions. For this work, 0.1 ml of solution was put into the porous cup by means of a small-bore pipette and excited by a high-voltage condensed spark.

##### TRIAL CALIBRATION WITH CHEMICALLY ANALYSED SAMPLES—

A series of analysed samples was selected from our laboratory stock to provide a range of 3 to 35 per cent. of copper, 3 to 37 per cent. of iron and 0.5 to 7 per cent. of cobalt. Solutions of each of these standards, prepared as before, were excited under the following conditions—

*Lower electrode*—A  $\frac{1}{4}$ -inch diameter graphite rod pointed to an 80° blunt cone.

*Upper electrode*—0.1 ml of sample solution in a Feldman porous cup.

*Spark gap*—3 mm.

*Condensed spark*—15 kV; 0.005  $\mu$ F.

*Exposure*—60 seconds on Kodak B10 plate (recorded in triplicate).

*Line pairs*—Cu II 2369.88 A - Ni II 2356.41 A  
 Co II 2353.42 A - Ni II 2356.41 A  
 Fe II 2359.10 A - Ni II 2356.41 A.

The choice of line pairs was rather arbitrary in the absence of excitation potential tables. However, care was taken to select lines of the same order, *i.e.*, in this instance “spark” lines, and of suitable density. The initial choice proved to be most fortunate, as a test for homology made by photographing spectra at inductances of 0.015, 0.03 and 0.06 mH showed no marked change in log intensity ratio with change of inductance. In practice, the line pairs were found to be reliable and gave adequate accuracy.

## STANDARDISATION—

Standard graphs for copper, cobalt and iron were plotted from the relevant photometric measurements of the selected line pairs, the points plotted being the mean values obtained from seven standard samples each exposed three times on each of two photographic plates.

## TRIAL ANALYSES OF COBALT CONCENTRATES—

At this stage it seemed possible to carry out trial analyses by the proposed method, and six cobalt concentrates were selected at random from routine plant production. These were analysed by comparative chemical and spectrochemical methods; the results are given in Table I.

TABLE I

## COMPARISON OF RESULTS BY CHEMICAL AND SPECTROCHEMICAL METHODS

Copper found by—		Iron found by—		Cobalt found by—	
chemical method, %	spectrochemical method, %	chemical method, %	spectrochemical method, %	chemical method, %	spectrochemical method, %
14.28	14.30	16.90	17.15	4.88	5.40
13.78	14.05	16.20	16.60	4.59	4.85
14.14	14.30	16.60	17.20	4.74	5.15
14.10	14.30	16.75	16.70	4.82	5.25
14.06	13.90	16.80	17.05	4.96	5.10
14.12	14.40	16.80	17.15	4.88	5.30

It can be seen from the results in Table I that chemical and spectrochemical results for copper and iron show good agreement, but those for cobalt (with one exception) do not.

The samples used for the spectrochemical analysis were then analysed chemically by an umpire method, while the spectrochemical solutions were again analysed, use being made of a calibration graph obtained from a series of pure solutions containing from 1 to 6 per cent. of cobalt. The results from both chemical and spectrochemical methods are shown in Table II.

TABLE II

## DETERMINATION OF COBALT BY DIFFERENT METHODS

Cobalt found by chemical method, %	Cobalt found by umpire's chemical method, %	Cobalt found by spectrochemical method, %	Cobalt found previously by spectrochemical method, %
4.88	5.03	5.10	5.40
4.59	4.57	4.70	4.85
4.74	4.88	4.90	5.15
4.82	4.87	4.90	5.25
4.96	4.95	5.0	5.10
4.88	4.97	5.05	5.30

In view of the good agreement finally achieved, a further series of cobalt concentrates was analysed, use still being made of the calibration graph for cobalt. Comparative chemical and spectrochemical results on these samples are given in Table III.

TABLE III

## COMPARISON OF RESULTS BY CHEMICAL AND SPECTROCHEMICAL METHODS

Copper found by—		Iron found by—		Cobalt found by—	
chemical method, %	spectrochemical method, %	chemical method, %	spectrochemical method, %	chemical method, %	spectrochemical method, %
13.72	13.70	16.50	16.55	4.72	4.80
14.10	14.20	16.90	16.90	5.14	5.00
13.82	13.70	16.35	16.20	4.72	4.60
14.00	13.95	16.90	16.90	5.10	5.00
13.76	13.35	16.35	16.20	4.64	4.70
14.12	13.70	16.75	16.90	4.98	5.00

*Calibration by synthetic solution standards*—In view of the success attained with the calibration graph for cobalt, it was felt that a complete calibration by synthetic solution standards for copper, iron and cobalt was desirable, since it would dispense completely with the need for accurately analysed standard samples.

Initial trials with this form of calibration soon showed that solutions containing only the pure metals themselves were not sufficient—to these solutions must be added weighed amounts of lime, magnesia, alumina and sodium equivalent to the concentrations normally present in the concentrates.

#### REPRODUCIBILITY OF RESULTS BY THE SPECTROCHEMICAL METHOD—

After a calibration graph had been prepared for copper, iron and cobalt from the synthetic solutions, a series of replicate analyses of a copper and a cobalt concentrate was carried out. These analyses were spread over a total of eight photographic plates exposed at intervals during a period of 1 month. Standard samples were not exposed on any of the plates. From the results of the replicate analyses the reproducibility of the results by the spectrochemical method was calculated statistically, with the results shown in Table IV.

TABLE IV  
REPRODUCIBILITY OF RESULTS

	Cobalt concentrate			Copper concentrate		
	Copper	Iron	Cobalt	Copper	Iron	Cobalt*
Found by chemical analysis, % ..	12.68	18.45	4.96	37.34	14.40	0.23
Found by spectrochemical analysis (mean), % .. ..	12.6	18.6	5.0	36.6	14.5	0.23
Standard deviation, % .. ..	±0.22	±0.27	±0.08	±0.93	±0.18	±0.018
Standard deviation, % of chemical content .. ..	1.74	1.46	1.61	2.5	1.25	7.83
Number of determinations ..	25	25	25	25	23	25

\* The determination of low concentrations of cobalt requires the use of stronger sample solutions and a longer exposure time, see p. 133.

#### METHOD

##### REAGENTS—

*Bromine*—Analytical-reagent grade.

*Nitric acid, concentrated.*

*Hydrochloric acid, concentrated.*

*Hydrofluoric acid, 40 per cent.*—Analytical-reagent grade.

*Perchloric acid, 60 per cent.*—Analytical-reagent grade.

*Standard nickel solution*—Dissolve 5 g of Specpure nickel in 15 ml of nitric acid, cool and make up to 100 ml in a calibrated flask.

1 ml ≡ 0.05 g of nickel.

*Standard cobalt solution*—Dissolve 0.1 g of Specpure cobalt sponge in 10 ml of nitric acid, cool and make up to 100 ml in a calibrated flask.

1 ml ≡ 0.001 g of cobalt.

##### PROCEDURE FOR DECOMPOSING THE CONCENTRATES—

Weigh 0.5 g of sample into a 400-ml Phillips conical beaker, moisten with a little distilled water, and add a few drops of bromine and 5 ml of concentrated nitric acid. Allow the sample to digest on a hot-plate at medium heat until all bromine and nitrous fumes are expelled. Add 5 ml of concentrated hydrochloric acid and proceed with digestion until further visible reaction ceases. Add 1 ml of hydrofluoric acid and 10 ml of perchloric acid, and continue heating until visible reaction ceases.

By increasing the heat, evaporate the contents of the beaker to a paste. Cool and add 5 ml of concentrated hydrochloric acid, washing down the sides of the beaker with a little distilled water. Heat until all salts are re-dissolved, cool and make up to 25 ml in a calibrated flask. These operations should take 30 to 35 minutes.



## PROCEDURE FOR PREPARING THE SOLUTION FOR ANALYSIS—

(i) Allow the sample solution to stand for 3 to 5 minutes to permit the small amount of residue to settle.

(ii) For the determination of copper and iron in the range 3 to 40 per cent., and cobalt in the range 1 to 6 per cent., add by means of a pipette 5 ml of sample solution to a 50-ml flat-bottomed flask and then, by pipette, 1 ml of standard nickel solution.

(iii) For the determination of low cobalt contents over the range 0.15 to 1.0 per cent., add by means of a pipette 10 ml of sample solution to a 50-ml flat-bottomed flask and then, by pipette, 1 ml of standard nickel solution.

TABLE V  
COMPOSITION OF STANDARDS BASED ON 1-g SAMPLE

Standard number	1	2	3	4	5	6
Copper present, %	5.0	8.0	13.0	20.0	30.0	40.0
Weight of copper taken, g	0.05	0.08	0.13	0.20	0.30	0.40
Iron present, %	5.0	8.0	13.0	20.0	30.0	40.0
Weight of iron taken, g	0.05	0.08	0.13	0.20	0.30	0.40
Cobalt present, %	1.0	2.0	3.0	4.0	5.0	6.0
Weight of cobalt taken, g	0.01	0.02	0.03	0.04	0.05	0.06
Aluminium oxide present, %				3.0		
Weight of aluminium oxide taken, g				0.03 ± 0.001		
Magnesium oxide present, %				3.0		
Weight of magnesium oxide taken, g				0.03 ± 0.001		
Calcium oxide present, %				2.0		
Weight of calcium carbonate taken, g				0.036 ± 0.001		
Sodium present, %				1.0		
Weight of sodium chloride taken, g				0.025 ± 0.001		

## PROCEDURE FOR PREPARING SYNTHETIC SOLUTION STANDARDS—

(a) For copper and iron between 5 and 40 per cent. and cobalt between 1 and 6 per cent.—Weigh into 400-ml Phillips conical beakers the respective amounts (based on a 1-g sample) of Specpure copper, cobalt and iron and the oxides and salts of aluminium, magnesium, calcium and sodium as shown in Table V.

Dissolve each standard mixture as described for the decomposition of the concentrates, finally adding 10 ml of concentrated hydrochloric acid and diluting to 50 ml in a calibrated flask. Add 5 ml of each standard solution to 1 ml of standard nickel solution as described previously.

(b) For cobalt between 0.20 and 1.0 per cent.—Weigh into each of five 400-ml Phillips conical beakers the amounts of aluminium oxide, magnesium oxide, calcium carbonate and sodium chloride given in Table V, and 0.35 g of Specpure copper and 0.15 g of Specpure iron.

To each mixture add, from a microburette, the volume of standard cobalt solution required to give, successively, 0.20, 0.40, 0.60, 0.80 and 1.0 per cent. of cobalt, *i.e.*, 2, 4, 6, 8 and 10 ml, respectively.

Dissolve each mixture as described for the decomposition of the concentrates, the final solution being made up to 50 ml with 20 per cent. v/v hydrochloric acid. Add, by pipette, 10 ml of each standard solution to 1 ml of the standard nickel solution.

## PROCEDURE FOR RECORDING THE SPECTROGRAMS—

The spectrographic and photographic data used for recording the spectrograms are given in Table VI.

*Plate calibration*—Routine plate calibration practice in this laboratory requires the individual calibration of each plate.

Briefly, the procedure is similar in principle to that previously recommended by McK. Nobbs and Beale,<sup>8</sup> the value of gamma for each plate being derived from an iron-spark spectrum recorded on that plate; the group of iron lines used, together with their relative intensity values, are given in Table VII.

The particular deflection - relative intensity Table for that value of gamma is then selected from a series of such Tables compiled from a family of plate-response curves prepared to cover the range of gamma values experienced in normal practice. Kaiser - Seidel

transformations<sup>9</sup> (P values) are applied to straighten each of the plate-response curves, from which are drawn the Tables.

TABLE VI

## SPECTROGRAPHIC AND PHOTOGRAPHIC DATA

Spectrograph .. .. .	Hilger large-quartz fully automatic
Slit width .. .. .	15 $\mu$
Slit length .. .. .	1.75 cm
Source to slit distance .. .. .	36 cm
Condensing lens .. .. .	F.1025
Wavelength region .. .. .	2230 to 2900 A
Lower electrode .. .. .	$\frac{1}{4}$ -inch diameter graphite rod (A.R.L. standard grade) pointed to 80° blunt cone
Upper electrode .. .. .	Porous cup—a $\frac{1}{8}$ -inch diameter hole drilled to within 1 mm of the end of a 0.7-inch length of $\frac{1}{4}$ -inch diameter graphite rod. The base is first rendered porous by heating to dull redness in a blow-pipe flame. A 0.1-ml portion of the analysis solution is placed in the cup from a small-bore pipette
Spark gap .. .. .	3 mm
Method of excitation .. .. .	High-voltage condensed spark
Nominal secondary voltage .. .. .	15 kV, r.m.s.
Capacitance .. .. .	0.005 $\mu$ F
Added inductance .. .. .	Nil
Exposure: (a) For the determination of Cu, Fe and Co in Co concentrates, and Cu and Fe in Cu concentrates .. .. .	60 seconds (triplicate exposures on each solution)
(b) For the determination of Co in Cu concentrates .. .. .	2 superimposed exposures of 75 seconds each (duplicate exposures on each solution)
Photographic plate .. .. .	Kodak B.10
Plate processing .. .. .	2 $\frac{1}{2}$ minutes' development at 20° C followed by fixing in acid fixer for 1 minute, washing in running water for 3 minutes and drying in a current of warm air
<i>Developer formula—</i>	
Metol (Kodak) .. .. .	1 g
Hydroquinone .. .. .	2.2 g
Sodium sulphite, anhydrous .. .. .	13.0 g
Sodium carbonate, anhydrous .. .. .	9.0 g
Potassium bromide .. .. .	0.3 g
Distilled water to .. .. .	1000 ml
Densitometer .. .. .	Hilger non-recording, optical magnification $\times 10$
Slit width .. .. .	0.13 mm
Slit length .. .. .	1.5 cm
Clear-glass deflection .. .. .	50 cm (full-scale)
Line pairs (M.I.T. wavelengths)—	
Cu II 2369.887 - Ni II 2356.41 .. .. .	Range 5 to 40% Index value* 11%
Fe II 2359.104 - Ni II 2356.41 .. .. .	5 to 40% 14%
Co II 2353.42 - Ni II 2356.41 .. .. .	(a) 1 to 6% 4.5%
	(b) 0.20 to 1% C

C = beyond range of graph.

\* The index value is the concentration of the element being determined at which the intensities of the analytical and internal standard lines are equal, *i.e.*, log intensity ratio = 0.0.

TABLE VII

## IRON-SPARK CALIBRATION LINES

M.I.T. wavelength, A	Relative intensity
2793.888	1.40
2799.286	1.00
2812.493	0.16
2819.333	0.19
2827.434	0.45
2828.634	1.06

*Standardisation*—The six standard solutions were each exposed three times on each of three plates spread over a period of 1 week. From the spectra of the standard solutions

the densitometer deflection readings of the line pairs were obtained. These values were converted to log relative intensity values by reference to the relevant plate calibration data, and, from these intensity values, the log intensity ratios  $I_{Cu}/I_{Ni}$ ,  $I_{Co}/I_{Ni}$  and  $I_{Fe}/I_{Ni}$  were found.

The mean value for a line pair for each sample was then calculated and standard graphs for copper, cobalt and iron were constructed by plotting this mean log intensity ratio against log percentage concentration.

Typical graphs are shown in Figs. 1 and 2. These graphs have been found to be remarkably constant and it has not been necessary to include spectra of standard samples on the same plate as unknown samples.

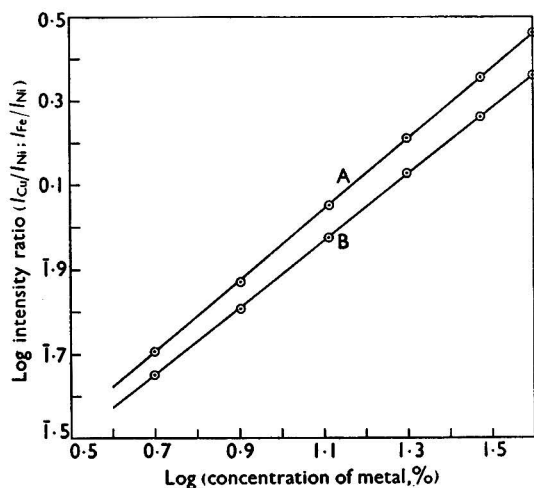


Fig. 1. Standard curves for copper and iron in copper and cobalt concentrates: curve A, Cu 2369.8 - Ni 2356.4; curve B, Fe 2359.1 - Ni 2356.4

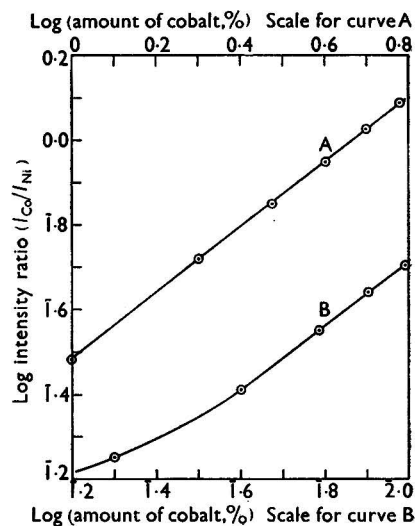


Fig. 2. Standard curves for cobalt in copper and cobalt concentrates with Co 2353.4 - Ni 2356.4 line pair: curve A, 1.0 to 6.0 per cent. of cobalt (cobalt concentrates); curve B, 0.20 to 1.0 per cent. of cobalt (copper concentrates)

**Evaluation**—From the spectra of the concentrate solution the mean log intensity ratios of the line pairs were obtained in the manner described. These values were then referred to the corresponding standard graph and the concentrations of copper, cobalt or iron were read.

#### SPEED OF ANALYSIS

With practice, one operator can analyse a single sample in 1 hour, and a batch of 20 samples in a working day.

We thank the Consulting Metallurgist, Anglo - American Corporation of South Africa Limited, for permission to publish this paper. We also express our appreciation for the collaborative chemical analyses carried out by colleagues of the analytical staff of the Research and Development Division.

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## A Spectrographic Method for the Determination of Rarer Elements in Silicates

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A general method for the determination of rarer elements in silicate rocks and minerals is described. Calcium sulphate is used as the spectrographic buffer and internal standard, the source of energy being a d.c. carbon arc.

MANY rarer elements are detectable by spectrographic methods in silicate rocks and minerals. The literature of the subject is extensive: information concerning their own work and the work of others has been summarised by Mitchell<sup>1</sup> and by Ahrens.<sup>2,3</sup>

In the development of the general method described later, the aim has been applicability to specimens that have widely different major constituents and a compromise between simple direct methods and the more accurate methods, in which a selected internal standard is added for the element to be determined.

The features of the proposed method are as follows—

- (i) Its general suitability for silicate rocks and minerals.
- (ii) The provision for estimations by visual inspection of the photographic plate and for photometric determinations of elements that are sometimes present in relatively large amounts, *e.g.*, chromium, nickel and vanadium.
- (iii) Some measure of control is achieved by using an internal standard.

In order to provide for (i) and (iii), the sample is buffered with calcium sulphate,\* which, at the temperature of the arc, will rapidly decompose the minerals in the sample and, being relatively involatile, will persist in the arc gases until the "burn" is completed. This dilution with calcium sulphate helps to stabilise the excitation conditions and to reduce the effects of variations in the major constituents of the samples, and also provides an expedient whereby valid corrections for impurities in the carbon electrodes can be made: as is well known, the detection of impurities in electrodes is sometimes stimulated when the arc contains added mineral matter.

To facilitate (ii), the spectra are stepped by using a rotating stepped sector, a device that also greatly widens the ranges of element concentrations determinable by a single exposure.

### PHOTOMETRIC DETERMINATIONS

The calcium-atom line at 3140.78 Å is used as the internal-standard control line, comparison with the analysis lines being made at constant photographic density. At a suitable density, the linear separations of the curves for density against the log of the relative exposure for the calcium and analysis lines are measured and correlated with percentages by means of a working curve, *e.g.*, Fig. 1 (a). A nomogram has been constructed to facilitate the calculation of Seidel densities.

The requirements for an ideal internal-standard spectrographic technique include the use of pairs of lines known to respond similarly to changes in excitation conditions, of element pairs of similar volatility, of lines free from self-absorption and of line pairs of similar wavelengths. Ideal requirements cannot be satisfied in a general method, but the use of the calcium line at 3140.78 Å provides some measure of control by internal standard, is practicable for a general method and is preferable to a direct method without an internal standard. Photographic processing conditions must be carefully standardised in order to minimise the effects of variations of plate gamma with wavelength.

\* Since the work described in this paper was completed, Turekian, Gast and Kulp<sup>4</sup> have shown that, for strontium determinations in silicates, the effects of varying matrix are reduced by adding calcium carbonate. Their figures for the strontium contents of two standard rock powders are similar to figures obtained by us for the same powders.

The presence of different amounts of calcium in the rock or mineral specimens will cause only slight variations in the density of the calcium line at 3140.78 Å. For specimens containing up to 10 per cent. of CaO, errors arising from this source are small, and the provision of a series of working curves for a range of calcium contents is normally not necessary.

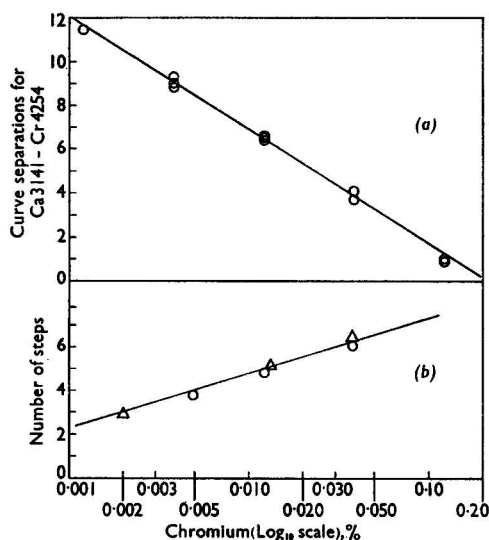


Fig. 1. Calibration curves for determinations of chromium by using the Cr 4254 line; (a) photometric method; (b) step-counting method. With (O) synthetic base and (Δ) rock-powder base

#### CORRECTION FOR BACKGROUND—

Corrections for the background produced by continuous radiation are made by using the ratio of the galvanometer deflections for "background" and for "line plus background" to calculate the photographic density of the line freed from background. Although it is not strictly valid, this method of correction appears to serve quite well for a general spectrographic method when a buffer is used.

#### VISUAL ESTIMATIONS

Estimations are made by counting the number of steps in which an image of the element line is visible, with fractional estimations of the density of the weakest step, *e.g.*,  $3\frac{1}{4}$ ,  $3\frac{1}{2}$ ,  $3\frac{3}{4}$  or 4 steps for a line visible in the fourth step, but not in the fifth step. The visual comparison of stepped spectrograms has been used by earlier workers.<sup>5,6,7</sup>

For any chosen element line, a count of the number of steps provides a relative inverse measure of the exposure necessary to produce a visible image, and is related to the intensity of emission. A rectilinear relationship between "number of steps" and "log, %," which should apply if reciprocity and intermittency effects are negligible, has been found to be valid for many of the calibratory plots actually obtained, *e.g.*, Fig. 1 (b). The calcium line at 3140.78 Å, used as the control line for photometric determinations, can also be used to correct observations made by the visual step-counting method.

#### CORRECTION FOR BLANK DETERMINATIONS—

A blank spectrum, obtained by striking an arc in a mixture of calcium sulphate and carbon, is recorded on every plate, so that corrections can be applied as necessary, notably for the small amounts of vanadium sometimes present in the carbon electrodes. The blank spectrum also helps with the avoidance of pitfalls, such as the confusion of a line of an (OH) band with the bismuth line at 3067.7 Å. Dingle<sup>8</sup> states that this band often appears in the spectrum of an arc in moist air.

Correction for traces of an impurity in the carbon or calcium sulphate is difficult to apply in terms of weight or percentage when a similar correction must also be applied to

the standard spectra used for constructing the working curve, *i.e.*, the amount of the impurity that produces the blank response is not easily determinable.

For photometric determinations, which are usually made only when the element response is strong, correction for the small blank value should not be necessary.

For estimations made by the visual step-counting method, we find that a sufficiently exact correction can be made by deducting the "intensity value" of the blank determination. We define the "intensity value" of the image of a stepped spectrum line visible in 1, 2, 3, 4, 5, 6 or 7 steps, as, respectively, 1, 2, 4, 8, 16, 32 or 64 for a stepped sector having an exposure ratio of 2 to 1. As an example, for an element line visible in, say,  $3\frac{1}{2}$  steps, with a blank value of 1 step, the corrected "intensity value" is  $(6 - 1)$ , and the corrected number of steps is  $3\frac{1}{4}$ .

#### NOTES ON THE SPECTRUM LINES

Carefully selected spectrum lines, suitable for determinations of the rarer elements in silicate rocks and minerals, are listed in Table II, together with appropriate comments. Although many of the lines selected appear in Dingle's<sup>8</sup> lists of sensitive multiplets, the most sensitive line for any particular element has not always been chosen, either because interference by (CN) bands or by emission from another element is likely, or because the most sensitive line is not located within the chosen wavelength range, *i.e.*, 2750 to 4670 Å. Some elements have therefore been listed that will rarely be detected in silicate rocks, but the inclusion of these elements ensures that their presence in unexpectedly high amounts does not escape notice. The wavelengths quoted are based on those given by Harrison.<sup>9</sup>

Many of the lines chosen, being atom lines, call for the use of an atom line as internal-standard control line. Noteworthy exceptions are the zirconium lines at 3392 and 3438 Å, the beryllium lines at 3130 and 3131 Å and the niobium lines at 3163 and 3195 Å, all of which are ion lines and none of which responds well to correction by the calcium-atom line at 3140.78 Å.

#### SEPARATION OF LINES—

The variation of dispersion of a prism spectrograph with wavelength and the resolving power of the photographic emulsion are factors that affect the interference of one spectrum line with another of similar wavelength.

TABLE I  
SEPARATION OF SPECTRUM LINES

Wavelength, Å	Plate factors, Å per mm	Wavelength differences necessary to eliminate interference by one line with a near line,	
		Å	
2780	3.7	0.11	
3000	4.7	0.14	
3200	5.8	0.17	
3400	7.1	0.21	
3500	7.8	0.23	
3705	9.3	0.28	
3906	11.0	0.33	
4005	12.0	0.36	
4227	13.4	0.40	
4337	15.1	0.45	
4427	17.0	0.51	
4638	18.2	0.55	

TABLE II  
SELECTED SPECTRUM LINES

Element	Approximate minimum detectable, %	Wavelength of line used,* Å	Comments
Sb	0.06	2877.92	Ca line may produce slight blank value. Cr may sometimes interfere
As	0.1	2780.20 2860.45	Separable from Mn line at 2780.00 Å Ti line at 2860.28 Å should be separable if present

\* The lines used for the detection of the minimum percentages are given in *italics*.

TABLE II—*continued*

Element	Approximate minimum detectable, %	Wavelength of line used,* Å	Comments
Ba	0.001	3071.59 <i>4554.04</i>	Ca line produces slight blank value An ion line. Inseparable Cr line will not normally interfere. Carbon bandhead at 4553.1 Å
Be	0.001	3130.42 3131.07 3321.01 3321.09 3321.34	Both are ion lines. Avoid confusion with V line at 3130.27 Å and Ti line at 3130.80 Å  Weak Cr line at 3321.19 Å
Bi	0.01	2897.98 <i>3067.72</i>	Inseparable weak Mn line should not often interfere Line of (OH) band may produce blank value. Weak Fe line at 3067.94 Å
Cd	0.02	3261.06	Very weak Ca line just separable. Very weak V line not separable
Ce	0.2?	3194.83 3234.16 <i>3272.25</i>	Nb line at 3194.98 Å will interfere unless very weak. Very weak Ca line may produce slight blank value Inseparable lines of Pr, Zr, etc., are normally unlikely to interfere. Weak Cr line at 3234.06 Å. When strong, Ti and Fe lines interfere Inseparable lines of Zr, V, etc., are normally unlikely to interfere. Ti line at 3272.08 Å just separable, unless strong
Cr	0.0005	2780.70 2843.25 3021.56 <i>4254.35</i>	Weak Fe line not separable. Cr line only suitable for strong response An ion line
Co	0.002	3449.17 3449.44 <i>3453.51</i>	Weak Ti line not separable, but unlikely to interfere. Weak Cr lines at 3453.33 and 3453.74 Å
Cu	0.0003	2824.37 <i>3247.54</i> 3273.96	Inseparable Ag line will not normally interfere Mn line may interfere when Cu response is weak Ca line may produce slight blank value. <i>Cu lines at 3247 and 3273 Å are usually detectable in a blank determination</i>
Ga	0.002	2943.64 2944.18	Avoid confusion with Co line at 2943.48 Å. Inseparable Fe line will not normally interfere Avoid confusion with Ni line at 2943.91 Å and Fe line at 2944.40 Å
Ge	0.005	3039.06 3269.49	Very weak Ca line at 3039.21 Å Weak Fe line at 3269.24 Å
In	0.002	3039.36 <i>3256.09</i> 3258.56	Inseparable Fe line should usually be very faint. Avoid confusion with Co line at 3039.57 Å Inseparable Mn line often interferes. Avoid confusion with Fe line at 3255.89 Å Mn line at 3258.41 Å: presence of this line indicates interference of Mn with In line at 3256.09 Å
La	0.005	3245.12 <i>3337.49</i>	An ion line. Inseparable Ce line should not normally interfere An ion line. Inseparable Ce line should not normally interfere. Fe line at 3337.67 Å is separable
Pb	0.005	2833.07	
Li	0.04 (0.02 if Fe absent)	3232.61 <i>4602.86</i>	Sb line at 3232.50 Å will not normally interfere Usable only in absence of Fe
Mn	0.0005	2799.84 <i>2801.06</i> 2914.60 2925.57	Inseparable Zn line will not normally interfere
Mo	0.001	3170.35 3193.97	Inseparable weak Fe line will not normally interfere Inseparable V line may sometimes interfere. Weak Fe line at 3193.80 Å

\* The lines used for the detection of the minimum percentages are given in *italics*.

TABLE II—*continued*

Element	Approximate minimum detectable, %	Wavelength of line used,* Å	Comments
Ni	0.0007	2943.91	Inseparable Cu line will not normally interfere Avoid confusion with Ti line at 3380.28 Å Avoid confusion with Co line at 3446.09 Å Weak Fe line at 3453.02 Å may sometimes interfere
		<i>3012.00</i>	
		3380.57	
		3446.26	
Nb	0.005	3452.89	Both are ion lines. Inseparable Ce, W and V lines should not normally interfere
		3163.40	
Sc	0.002	<i>3194.98</i>	Inseparable weak Fe line will not normally interfere An ion line. Inseparable Ce line should not normally interfere. Avoid confusion with Fe line at 4247.43 Å. Heavy background
		3269.90	
Sr	0.001	4246.83	An ion line. Yb line at 3464.37 Å will not normally interfere Possible interference by Fe and Mn lines is rarely appreciable. Carbon bandhead at 4606.1 Å
		3464.46	
Ta	0.2	4607.33	Very weak Nb line at 3311.34 Å
		3311.16	
Tl	0.01	2767.87	
Th	0.03	2837.30	Inseparable Ce and Zr lines should not normally interfere Inseparable weak Cr line should not normally interfere. Avoid confusion with V line at 2870.55 Å Fe line at 2981.85 Å. Ce line at 2981.91 Å
		2870.41	
Sn	0.005	2982.05	Inseparable weak Mn and Cr lines should not normally interfere Sometimes not free from interference by Fe line at 2863.44 Å Inseparable weak Fe and Ce lines should not normally interfere
		2839.99	
		2863.33	
W	0.02	3175.02	Avoid confusion with Co line at 3174.91 Å. Inseparable weak Ce and Fe lines should not normally interfere
		2946.98	
U	>0.5	2882.74	Inseparable Ta line should not normally interfere Avoid confusion with weak Mn line at 2882.90 Å
		4362.26	
V	0.002	2914.93	An ion line. Inseparable weak Si and Fe lines will not normally interfere
		2924.03	
		2924.64	
		3183.41	
Y	0.001	4379.24	An ion line Inseparable Pr line will not normally interfere An ion line. Ti line at 3199.92 Å and Fe line at 3200.48 Å interfere when strong. Weak Ni line at 3200.42 Å will not normally interfere
		3200.27	
		3327.88	
Zn	>0.3	4643.70	Inseparable Ce and Sm lines will not normally interfere Useful only to confirm higher percentages of Y. Avoid confusion with Co line at 4644.32 Å and with Eu line at 4644.24 Å. Inseparable from Er, Pr, and weak Fe lines
		3345.02	
Zr	0.0007	3391.98	Weak Cr and Ti lines will not normally interfere An ion line. Inseparable weak Fe line should not normally interfere appreciably
		3438.23	
		3438.23	An ion line. Weak Fe line at 3438.31 Å will not normally interfere appreciably

\* The lines used for the detection of the minimum percentages are given in *italics*.

Under the conditions prescribed later in this paper, and with the particular spectrograph used, visual or photometric work is possible if the lines are not very strong and are not less than 0.03 mm apart. Table I shows the wavelength differences necessary to eliminate interference by one line with a near line.

#### REPRODUCIBILITY OF RESULTS

The figures quoted below illustrate the degree of reproducibility attained when the method was applied to a series of silicate rocks, the figures enclosed in each pair of brackets being replicate photometric determinations made on the same sample. The replicate determinations are not sufficiently numerous to justify the calculation of coefficients of variation. For comparison, results of chemical determinations of manganese, chromium and barium



are printed in *italics*: the accurate chemical determinations of manganese indicate a fair degree of true accuracy for the spectrographic determinations.

The chemical determinations of barium and chromium are only approximate.

Manganese, %—	(0-072, 0-065, 0-066, 0-069) <sup>a</sup> (0-018, 0-015, 0-016, 0-016) <sup>b</sup> (0-072, 0-072, 0-072, 0-066) <sup>c</sup> (0-080, 0-090, 0-090, 0-070) <sup>d</sup> (0-014, 0-017, 0-013, 0-011) <sup>e</sup> (0-09, 0-10, 0-10, 0-08) <sup>f</sup> (0-030, 0-030, 0-030, 0-031) <sup>g</sup> (0-11, 0-12, 0-12, 0-12) <sup>h</sup> (0-11, 0-14, 0-12, 0-12) <sup>i</sup> (0-13, 0-17, 0-17, 0-17) <sup>j</sup> (0-014, 0-016, 0-014, 0-019) <sup>k</sup> (0-11, 0-10, 0-10, 0-08) <sup>l</sup>
Barium, %—	(0-060, 0-070, 0-070, 0-04) <sup>d</sup> (0-060, 0-072, 0-070, 0-05) <sup>e</sup> (0-062, 0-070, 0-073, 0-05) <sup>f</sup> (0-048, 0-057, 0-057, 0-03) <sup>h</sup> (0-045, 0-049, 0-047, 0-04) <sup>i</sup> (0-020, 0-020, 0-020, 0-02) <sup>j</sup> (0-085, 0-095, 0-095, 0-06) <sup>k</sup> (0-020, 0-020, 0-020, 0-02) <sup>l</sup>
Chromium, %—	(0-015, 0-015, 0-017, 0-01) <sup>d</sup> (0-0069, 0-0074, 0-0067, 0-007) <sup>e</sup> (0-029, 0-029, 0-030, 0-03) <sup>h</sup> (0-030, 0-033, 0-030, 0-02) <sup>i</sup> (0-032, 0-035, 0-035, 0-02) <sup>j</sup>
Nickel, %—	(0-0060, 0-0050, 0-0060) <sup>d</sup> (0-0026, 0-0034, 0-0032) <sup>e</sup> (0-0070, 0-0070, 0-0070, 0-0060) <sup>f</sup>
Strontium, %—	(0-014, 0-014, 0-015) <sup>d</sup> (0-0066, 0-0078, 0-0066) <sup>e</sup> (0-047, 0-048, 0-047) <sup>f</sup> (0-002, 0-002, 0-002) <sup>g</sup> (0-082, 0-090, 0-096) <sup>h</sup> (0-067, 0-072, 0-064) <sup>i</sup> (0-030, 0-034, 0-032) <sup>j</sup> (0-017, 0-018, 0-017) <sup>k</sup> (0-17, 0-19, 0-20) <sup>l</sup>
Vanadium, %—	(0-0058, 0-0033, 0-0050) <sup>a</sup> (0-0066, 0-0056, 0-0062) <sup>c</sup> (0-019, 0-018, 0-020) <sup>d</sup> (0-0070, 0-0080, 0-0070) <sup>e</sup> (0-0093, 0-0087, 0-010) <sup>f</sup> (0-0087, 0-0080, 0-0087) <sup>m</sup> (0-017, 0-016, 0-015) <sup>h</sup> (0-021, 0-022, 0-021) <sup>i</sup> (0-030, 0-030, 0-030) <sup>d</sup> (0-035, 0-034, 0-033) <sup>i</sup>
Yttrium, %—	(0-0062, 0-0082, 0-0054) <sup>n</sup> (0-010, 0-011, 0-011, 0-013, 0-011) <sup>a</sup> (0-0031, 0-0043, 0-0050, 0-0058, 0-0055) <sup>c</sup> (0-013, 0-013, 0-014) <sup>d</sup> (0-0038, 0-0041, 0-0039) <sup>d</sup>
Zirconium, %—	Direct determinations, without internal standard. (0-10, 0-09, 0-11) <sup>a</sup> (0-022, 0-021, 0-022) <sup>b</sup> (0-09, 0-12, 0-11) <sup>c</sup> (0-027, 0-027, 0-026) <sup>d</sup> (0-025, 0-038, 0-023) <sup>e</sup> (0-021, 0-020, 0-023) <sup>d</sup> (0-005, 0-007, 0-007) <sup>n</sup> (0-032, 0-037, 0-033) <sup>i</sup> (0-012, 0-014, 0-012) <sup>o</sup> (0-012, 0-010, 0-018) <sup>m</sup> (0-009, 0-008, 0-008) <sup>o</sup> (0-020, 0-022, 0-021) <sup>h</sup> (0-016, 0-017, 0-016) <sup>i</sup>

*a* = gneiss

*b* = felsite

*c* = hornfels

*d* = schist

*g* = granite

*h* = camptonite

*i* = lamprophyre

*k* = granulite

*l* = diorite

*m* = tonalite

*n* = pegmatite

*o* = porphyrite

As indicated later in the description of the method, each plate carries a spectrum of a control mixture of known element contents. Although the original standard mixtures were made entirely from pure chemical compounds, the control mixtures were rock powders (a granite and a felsite) to which additions of compounds of rarer elements were made. The control determinations provide additional information about the reproducibility of the results: some figures obtained to date are listed below, the figures in *italics* being the amounts actually present.

Manganese, %—	0-24, 0-20 0-13, 0-12, 0-12, 0-11, 0-12 0-044, 0-048, 0-046, 0-055, 0-045, 0-050
Barium, %—	0-12, 0-14, 0-13, 0-13, 0-14 0-040, 0-044, 0-048, 0-043, 0-055, 0-057 The line used, Ba 4554A, is an ion line
Chromium, %—	0-12, 0-10, 0-10, 0-11 0-038, 0-042, 0-044
Nickel, %—	0-060, 0-060, 0-052, 0-055 0-019, 0-020, 0-018
Strontium, %—	0-12, 0-10, 0-11, 0-11, 0-12 0-040, 0-034, 0-036, 0-047, 0-047
Vanadium, %—	0-061, 0-051, 0-057, 0-060, 0-060, 0-051 0-030, 0-024, 0-025, 0-028 0-010, 0-006, 0-009, 0-010, 0-010
Yttrium, %—	0-022, 0-020, 0-019, 0-019 0-010, 0-015, 0-011
Zirconium, %—	Direct determinations, without internal standard 0-076, 0-072, 0-096, 0-10, 0-090, 0-10 0-039, 0-036, 0-037, 0-044 0-019, 0-027, 0-018, 0-018

#### LATITUDE—

The use of only one calcium line for internal-standard control of all the other element lines is an empirical device that should eliminate gross errors when operating conditions are carefully standardised. To obtain information about the effects of deliberate departure from the standard operating conditions, some determinations have been made at increased

and decreased current (13 amperes and 8 amperes, respectively), and with a reduced amount of arcing mixture in the anode (35 mg instead of 52 mg). The figures quoted below show the minima and maxima found, the figures in *italics* being the amounts actually present.

Manganese, %—	<i>0.13</i> , 0.10 to 0.12
Vanadium, %—	<i>0.030</i> , 0.022 to 0.028
Nickel, %—	<i>0.060</i> , 0.040 to 0.065
Chromium, %—	<i>0.12</i> , 0.080 to 0.11
Barium, %—	<i>0.12</i> , 0.070 to 0.17
Strontium, %—	<i>0.12</i> , 0.081 to 0.15
Zirconium, %—	<i>0.039</i> , 0.012 to 0.038 (not corrected by internal standard)

These experiments demonstrate the effects of major changes in the operating conditions, and indicate that inadvertent fluctuations, which will be relatively minor, are not likely to be a source of gross errors.

#### METHOD OF RECORDING THE SPECTRA

An outline of the method that was used for recording the spectra is as follows.

*Arcing mixtures*—One part by weight of the finely powdered sample is mixed with 3 parts of purified ignited calcium sulphate and 4 parts of powdered carbon. For the blank determinations, the same calcium sulphate and carbon powder are mixed in the ratio of 3 to 5.

*Electrodes*—Carbon rods of diameter 5 mm are used. The anode (bottom electrode) is drilled with a 3-mm diameter drill (a No. 32 carbon-steel drill was used) to a depth of  $\frac{1}{4}$  inch, and this cavity is completely filled with the arcing mixture (average weight about 50 mg), which is compacted by pressing with a steel rod during filling. The tips of both electrodes are flat, not tapered.

*Optics*—A Hilger - Littrow spectrograph,  $F_d$  170 cm, with a quartz prism and lens is used. The wavelength range used is 2750 to 4670 Å. An image of the arc is focused on a 4-cm horizontal mask attached to the collimating lens to exclude radiation from the electrode tips and to pass radiation from only the central  $\frac{2}{3}$  of the arc. A six-step rotating sector, of step ratio 2 to 1, is used to produce the stepped spectra. The slit width used is 0.010 mm.

*Plates*—Ilford Thin Film Half Tone ordinary plates (backed) are used and developed for  $4\frac{1}{2}$  minutes at 75° F in Ilford I.D.11 developer (M.Q. Borax), the temperature being controlled thermostatically.

*Arcing technique*—A d.c. arc with a 10-mm arc gap, the gap being maintained at 10 mm during the entire arcing period, is used with no pre-arcing. The technique is as follows—

- The arc is struck at 3 to 4 amperes, the electrodes being separated gradually to reduce any tendency for mechanical loss during the destruction of minerals.
- After 30 seconds, the current is increased to 6 to 7 amperes, this current being maintained for 15 seconds.
- The current is now increased to  $10\frac{1}{2}$  amperes and arcing is continued "to completion," and thereafter for 10 seconds. "Completion" is indicated by a sudden change in the character of the arc accompanied by a fall in current of about 2 amperes. The total time of arcing is about 4 to  $4\frac{1}{2}$  minutes. The current is controlled by means of a tapped resistance, sections of which are shorted by switches to effect the desired increases in current. The maximum current is adjusted before making the exposures by setting a variable resistance to pass a current of 8.6 amperes with a 10-mm arc between plain 5-mm carbon rods.

*Exposure, etc.*—The plate is exposed during the entire period of arcing. Each plate carries spectra in triplicate of the sample, a spectrum of a control mixture of known element contents and a blank spectrum.

*Preparation of purified calcium sulphate*—The pure calcium sulphate normally obtainable often contains traces of strontium and barium. Calcium sulphate free from these metals has been prepared by the following method.

Suspend 100 g of AnalaR calcium carbonate in about 500 ml of water and dissolve by adding 250 ml of concentrated hydrochloric acid. Dilute to about 1300 ml and precipitate about 90 per cent. of the calcium by adding to the boiling solution a hot aqueous solution containing 130 g of ammonium oxalate. After an interval of 15 minutes, add a little filter-paper pulp and filter through a large Buchner funnel, washing the precipitate once with hot water.

Disperse the cake of calcium oxalate in about 500 ml of hot water, heat the beaker on a steam-bath, and add concentrated hydrochloric acid gradually until dissolution is complete. Re-precipitate the calcium oxalate from the near-boiling solution by adding slowly, with constant stirring, a hot 9 N solution of ammonia. When the neutral point to methyl orange is reached, slightly acidify the solution by adding 20 drops of concentrated hydrochloric acid. Filter and wash the precipitate as before. Again re-precipitate in a similar manner.

Convert the calcium oxalate to oxide and destroy organic matter by ignition at a temperature of about 900° C in a platinum basin, slake by the cautious addition of water, and convert to sulphate by adding a slight excess of diluted sulphuric acid (1 + 1). Evaporate on a steam-bath and drive off the excess of sulphuric acid by heating at the fuming-point. Ignite the calcium sulphate at 900° C for about 1 hour and mix thoroughly. This calcium sulphate does not hydrate when exposed to a moist atmosphere.<sup>10</sup>

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## Determination of Water in Granulated Sugar

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Water in granulated sugar can be determined by grinding and drying the sample in a vacuum. Steel balls are used to grind the sample to a fineness of 3500 sq. cm per g and drying is carried out at 60° C for 15 hours. The water vapour evolved is collected and measured by observing the pressure exerted by it in a known volume.

Tests have shown that the water in granulated sugar, usually about 0.04 per cent., can be determined with a coefficient of variation of less than 1 per cent. Comparisons have been made with other methods and the distribution of water between the surface and the interior of sugar crystals has been investigated.

A METHOD for the accurate determination of the water content of granulated sugar (sucrose) is required for several reasons. Apart from the necessity of accurately analysing the output of granulated sugar from a sugar refinery, it is necessary to obtain a precise analysis of the sucrose that is used for the standardisation of saccharimeters, refractometers, etc. This analysis must include an estimate of the water content. Sucrose that is used for calibration purposes can be previously dried, but it may take up an unknown amount of water from the atmosphere during weighing and other operations before dissolution. A sounder method for purposes of standardisation is to allow the sucrose to come into equilibrium with the humidity in the atmosphere and to measure, and allow for, the amount of water in the sample.

It can be safely stated that no satisfactory method of determining the water content of crystalline sucrose has previously been described. It is usually determined by measuring

the loss of weight from a sample of about 20 g when it is heated at 105° C in air at atmospheric or reduced pressure.<sup>1</sup> It is generally recognised that, at this temperature, a certain amount of slow decomposition occurs, so a limit must be placed on the time of dehydration. As the total water content of a typical granulated sugar is of the order of 0.04 per cent., the amount of decomposition that can be tolerated is very small. An illustration of the uncertainty that exists on this subject is that different drying times of from 30 minutes to 3 hours have been recommended. Drying to constant weight is not sound, firstly on account of decomposition, and secondly because the regain of moisture during weighing eventually cancels the loss during the intervening periods of dehydration.

It will be shown later that approximately half the water in granulated sugar is contained within the structure of the sugar crystals. A serious objection to the conventional method for determining water is the inaccessibility of this water, unless the crystals are finely ground. However, when the crystals are ground in air, there may be an unknown exchange of water between the newly created surfaces and the atmosphere before the sample can be weighed. Certain properties of granulated sugar depend primarily on the amount of the surface moisture. One such property, for example, is caking of the sugar during storage. This can be caused by migration of water on account of temperature gradients. External moisture can be determined by the conventional method, but the limits of error are rather wide. The proposed method, although developed primarily for total water, can also be used, by omitting the grinding, to determine external moisture only, and it is much more accurate than the conventional method.

The proposed method for determining water is not, in its present form, entirely suitable for routine analysis. It is intended mainly for use when a relatively elaborate procedure is justified and also as a standardising method, to which other more rapid procedures may be referred.

#### VACUUM DETERMINATION OF WATER

About 15 g of the sugar under test are sealed in a thin glass ampoule, which is then enclosed in a flask that can be evacuated. After evacuation of the flask, the ampoule is broken, the sugar is finely ground *in situ* and the water is driven from the sample and condensed in a second evacuated space of known volume. This space is then sealed and the condensed water is allowed to evaporate. The amount of water is indicated by the pressure exerted by the vapour in the known volume.

This method for determining water has previously been used for certain other materials, *e.g.*, paper,<sup>2</sup> and a form of apparatus for this type of procedure is commercially available, but the adaptation of the method for use with granulated sugar required certain special features, which are described later.

#### METHOD

##### APPARATUS—

The vacuum system is shown in Fig. 1, which is drawn approximately to scale. About 15 g of sugar are sealed in the previously dried ampoule, P. Care must be exercised while sealing the ampoule to prevent any over-heating of the sugar. If any caramelisation occurs the sample must be rejected, otherwise cumulative decomposition will take place during the subsequent heating and the result will be incorrect. For this reason the ampoules are made from soft (soda or lead) glass. The ampoule is supported in the neck of the flask, A, by means of a glass rod, B, which is free to slide in a side arm of the flask. Inside the flask are four  $\frac{3}{8}$ -inch diameter stainless-steel balls, which are later used to break the ampoule and to grind the sugar. The flask is attached to the rest of the vacuum system by way of a conical joint, C, which is sealed with Picien wax, a tap, D<sub>1</sub>, and a spherical ground joint, E. A condensing tube, F, is sealed on at the level of tap D<sub>1</sub>.

The known volume in which the water is collected is the section bounded by taps D<sub>2</sub> and D<sub>3</sub>, and by the Apiezon oil in the left-hand member of the manometer, M. This section includes a U-shaped cold trap, T, and a bulb, K, which has been added to increase the volume to a convenient value for a 15-g sample, *i.e.*, approximately 300 ml. To the right of tap D<sub>3</sub> in the diagram are a McLeod gauge and an oil diffusion pump. The gauge is convenient rather than necessary. If a good quality two-stage rotary pump is available, the diffusion pump is probably unnecessary also.

Other items required are a vernier telescope for reading the manometer, a thermostatically controlled heater, L, in which the flask is heated, and a shaking machine. A number of flasks can be attached simultaneously to the vacuum system. We have used four flasks; the practical maximum is probably about twelve.

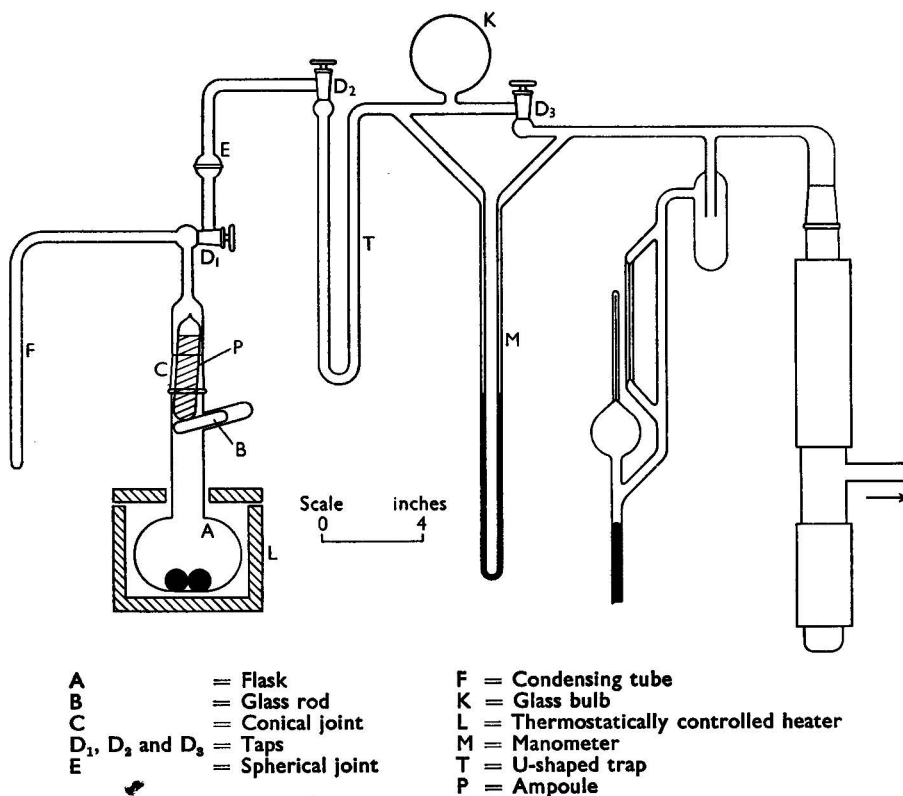


Fig. 1. Apparatus for determining water in granulated sugar

#### PROCEDURE—

With taps  $D_1$ ,  $D_2$  and  $D_3$  open, flask A is heated at  $120^\circ\text{C}$  for  $\frac{1}{2}$  hour under vacuum to eliminate stray moisture and a flame is applied for a few seconds to the condensing tube. Taps  $D_1$  and  $D_2$  are closed and the flask is detached from the vacuum system at joint E. The polished steel balls, in a good vacuum, and making only single point contact with the wall of the flask, cool very slowly. A period of  $\frac{3}{4}$  hour must be allowed for cooling before the ampoule is broken by dropping it into the flask. The sugar is then ground by the steel balls for 1 hour by subjecting the flask to a circular motion in the shaking machine. The flask, which is mounted in the machine with its axis vertical, does not rotate. It performs a circular orbit 400 times per minute and its axis sweeps out a vertical cylinder of radius  $\frac{3}{8}$  inch. These conditions are not critical, but the grinding procedure should produce in the sugar a specific surface of not less than 3500 sq. cm per g. After reconnecting the flask to the vacuum system, the space between taps  $D_1$  and  $D_2$  is evacuated, but tap  $D_1$  remains closed. The condensing tube is cooled in a mixture of solid carbon dioxide and ethanol and the water is driven from the sugar by heating the flask at  $60^\circ\text{C}$  for 15 hours. Justification for the choice of 15 hours will be given later. Before discontinuing the heating, tap  $D_3$  is closed and the refrigerant is transferred to the cold trap and tap  $D_1$  is opened. By cooling the trap (at least 6 inches of which should be immersed) before opening tap  $D_1$ , condensation is made to take place mainly in the left hand member of the trap in the neighbourhood of the "water line." Although ice has an appreciable vapour pressure at  $-72^\circ\text{C}$ , the loss of water by diffusion through the trap is below the detectable limit. After the application of a flame to the condensing tube, tap  $D_3$  is opened for  $\frac{1}{2}$  minute to eliminate the

air that has been liberated from the ampoule. Finally, taps  $D_1$ ,  $D_2$  and  $D_3$  are closed and the refrigerant is removed. When equilibrium is reached, the vapour pressure of the water is read on the manometer. The volume occupied by the vapour must be large enough to keep the vapour pressure below the saturation value, *i.e.*, 14.5 mm of mercury at 17° C.

During the course of the early experiments, the grinding technique was such that the sugar was spread in a thin adhesive layer over the inner surface of the flask. When the sugar samples were heated, a white distillate accumulated as a film in the part of the neck of the flask that was outside the heater. Also, hourly tests showed that the evolution of water settled down after a few hours to a relatively high constant rate, presumably owing to decomposition of the sugar. No distillate was formed unless the sugar was ground *in situ*. If the sugar was not ground, or if it was ground in a mortar and then put into the flask, the distillate did not appear. It seems that a reaction can occur between the sugar and the flask, which was originally made of Pyrex glass. The difficulty was eventually overcome by using flasks of Monax glass of the shape and size shown in Fig. 1, and by grinding as described, so that a thin layer of sugar is not formed. In view of the small difference between the chemical constitutions of Pyrex glass and Monax glass, the improvement was probably due to the change in the grinding technique.

#### CALCULATION OF RESULTS—

The percentage of water ( $p$ ) in the sample is given by—

$$p = \frac{18.02}{22.4} \times \frac{273}{(273 + t)} \times \frac{Vh\rho}{76 \times 13.6} \times \frac{100}{M}$$

where  $V$  = the calibrated volume in litres,  
 $h$  = the manometer reading in cm,  
 $\rho$  = density of the oil in the manometer in g per ml,  
 $M$  = the mass of the sample in g, and  
 $t$  = the ambient temperature in °C.

As  $V$  and  $\rho$  are instrumental constants—

$$p = \frac{\text{constant} \times h}{M(273 + t)}$$

so that  $p$  can be read from a nomogram as a function of  $h$ ,  $M$  and  $t$ .

The following corrections must be applied to this result—

(a) An allowance must be made for the increase in  $V$  caused by the fall in the level of oil in the left-hand member of the manometer. Alternatively, the design of the manometer can be such that the oil level in the left-hand member can be restored to a fixed mark.

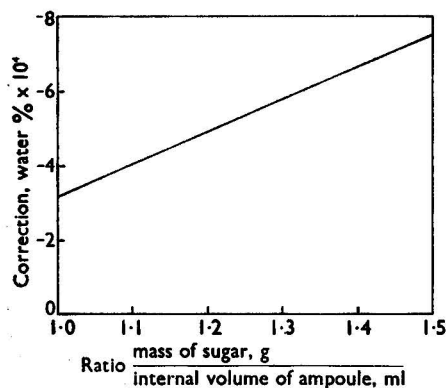


Fig. 2. Correction curve for water vapour in the air enclosed with the sample

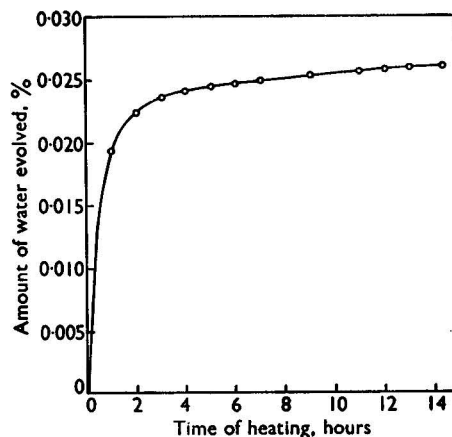


Fig. 3. Effect of time of heating on the evolution of water

(b) The air enclosed with the sample in the ampoule contains water vapour. Fig. 2 shows the correction to be applied if the enclosed air is assumed to have a relative humidity

of 50 per cent. at 20° C. As  $V/M$  need not exceed 1.25 ml per g, an error of 20 per cent. in the assumed relative humidity will introduce an error into the final result of less than  $\pm 0.0002$  per cent., *i.e.*, about 0.5 per cent. of the water to be expected in the sample.

#### TESTS OF THE METHOD

A number of observations have been made to test the validity of the method.

#### BLANK TESTS—

Any leakage of moist air into the apparatus and any moisture on the ampoule or in the flask will increase the result. Blank tests have shown that leakage is easily prevented and that, after the preliminary heating, stray moisture is negligible.

After the normal heating period in the vacuum apparatus, samples of sugar have been allowed to cool and observations have continued for 1 hour. No further evolution of water vapour has occurred during the extra hour.

#### CONTINUOUS OBSERVATION OF THE EVOLUTION OF WATER—

At any stage the amount of water driven off can be measured by transferring the water from the condensing tube to the cold trap. After measurement each increment of water is pumped away. Fig. 3 shows the result of such a procedure. After 14 hours the rate of evolution is less than 0.0001 per cent. per hour of the mass of sugar. Many other tests have confirmed this result.

#### EXAMINATION OF THE CONDENSATE—

There is a high probability that the substance condensed in the cold trap is water, but confirmation is desirable. Accordingly, the following tests were carried out—

(a) Exposure of the vapour to phosphorus pentoxide reduced the vapour pressure to 0.005 of its original value. A sample of the condensate was allowed to evaporate into a suitable optical cell and its infra-red absorption spectrum was recorded. Apart from the well developed absorption bands due to water, the only feature of the spectrum was a small peak at  $12.6 \mu$ . The height of this peak was not affected by exposure to phosphorus pentoxide. It follows that water vapour accounts for 99.5 per cent. of the total vapour pressure.

(b) A gravimetric method of determining water, based on a reaction with cobaltous bromide, has been developed by Gardiner and Keyte of this laboratory.<sup>3</sup> Their method was applied to an amount of condensate that was estimated by the vacuum method to consist of 9.80 mg of water. The mass of water in 9.80 mg of sample was found by

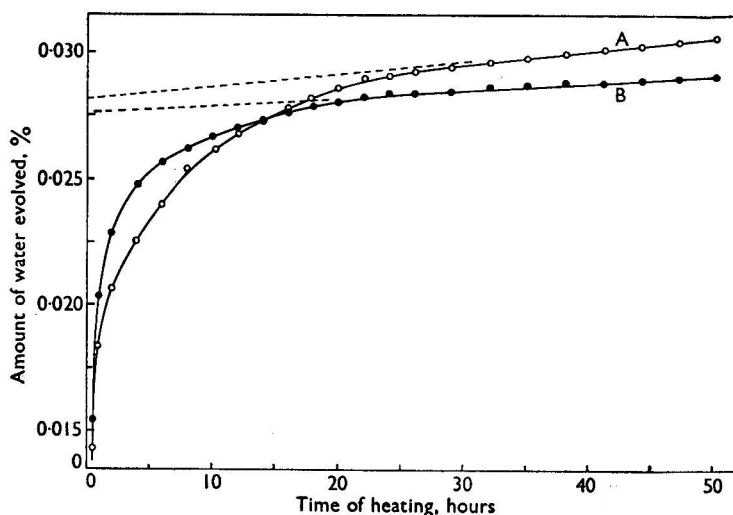


Fig. 4. Effect of prolonged heating on the evolution of water: curve A, at 90° C; curve B, at 60° C

the cobaltous bromide method to be  $9.6 \pm 0.5$  mg. Agreement is within the experimental error.

#### EFFECT OF PROLONGED HEATING—

Although the rate of evolution of water decreases to a very low figure after 15 hours, it was considered necessary to investigate the effect of further heating. Curve B of Fig. 4 shows that the rate of evolution eventually becomes constant. This may reasonably be attributed to decomposition of the sugar. Extrapolation of the linear portion of the curve back to zero time will then give the true initial water content. To an accuracy that is at present sufficient, *i.e.*,  $\pm 0.001$  per cent., this is the result obtained after 15 hours of heating. Greater accuracy can, of course, be achieved by the extrapolation procedure.

#### EFFECT OF TEMPERATURE OF DEHYDRATION—

In order to establish whether all the water is eliminated at  $60^\circ\text{C}$ , comparisons have been made between the results with similar samples at  $60^\circ$  and  $90^\circ\text{C}$ . Curve A of Fig. 4 shows the result of prolonged dehydration at  $90^\circ\text{C}$ . Back extrapolation of curves A and B gives 0.0281 and 0.0276 per cent. of water, respectively. Another comparison with a different sugar gave the following results—

Sample No. . . . .	1	2	3
Temperature of dehydration, $^\circ\text{C}$ . . . . .	90	90	60
Water, % . . . . .	0.0524	0.0520	0.0516

The agreement shown is within the limits of the sampling errors. It will be observed that the rate of decomposition indicated by the asymptotic slope of curve A in Fig. 4 is greater than that shown by curve B. An estimate of decomposition can be obtained by determining the final invert contents. The final inverts of the sample used to prepare curves A and B, determined by de Whalley's methylene blue test,<sup>4</sup> were 0.029 and 0.022 per cent., respectively. The initial invert, similarly measured, was 0.007 per cent.

#### STANDARD DEVIATION OF A MEASUREMENT—

In order to find the reproducibility of the results by the method, determinations were made on a series of 10 samples of ordinary granulated sugar. These samples were drawn from a 2-lb batch that had been kept in a sealed container for several days so as to establish uniform distribution of moisture. The results were as follows—

Sample No. . . . .	1	2	3	4	5	6	7	8	9	10
Water, % . . . . .	0.04135	0.04129	0.04154	0.04138	0.04143	0.04135	0.04152	0.04088	0.04193	0.04146

The standard deviation of the results is  $\pm 0.000260$  per cent. with a coefficient of variation of 0.63 per cent. To achieve this reproducibility very careful sampling is necessary.

#### DIRECT CALIBRATION OF THE APPARATUS—

Small weighed amounts of water were sealed into ampoules and were determined by the method. The results were as follows—

Sample No. . . . .	1	2	3	4	5	6	7	Total
Water taken, mg . . . . .	4.96	13.42	4.53	5.39	8.78	5.05	5.87	48.00
Water found, mg . . . . .	5.01	13.44	4.93	5.21	8.75	5.07	5.88	48.29

Except for sample No. 3, agreement is within the limits of accuracy of the weighing.

#### EFFECT OF GRINDING THE SUGAR—

To test the adequacy of the grinding procedure, four samples of granulated sugar were ground for periods of  $\frac{1}{4}$ ,  $\frac{1}{2}$ , 1 and 2 hours. The water determinations were then completed, the results being as follows—

Time of grinding, hours . . . . .	$\frac{1}{4}$	$\frac{1}{2}$	1	2
Specific surface, sq. cm per g . . . . .	1150	2500	3570	4500
Water found, % . . . . .	0.0201	0.0249	0.0314	0.0312

It can be seen that grinding for 1 hour is adequate. The specific surfaces were measured by the air permeability method.

#### WATER IN CRYSTALS OF GRANULATED SUGAR

During the crystallisation of sucrose, some water is retained inside the structure of the crystals.<sup>5,6</sup> The magnitude of this effect has been shown by comparisons of the amounts



of water evolved when the determination was made as described and when the grinding procedure was omitted. The results are shown in Table I. Sugars of three different mean apertures were used (mean aperture = aperture of a square-mesh sieve through which 50 per cent. of the sugar will pass). In addition, a sample of pure sucrose was tested. Pure sucrose receives extra washing in the centrifugal machine before granulation, so that the surface impurities have been reduced to the minimum possible. This is the sugar that is used for standardisation purposes.

TABLE I  
COMPARISON OF RESULTS ON GROUND AND UNGROUND SUGAR

Sugar	Mean aperture, inches	Water found in ground sample, %	Water found in unground sample, %
Liverpool No. 2 granulated ..	0.0360	0.0371	0.0055
Tate and Lyle ordinary granulated ..	0.0253	0.0202	0.0108
Caster .. .. .	0.0132	0.0299	0.0131
Pure sucrose .. .. .	0.0188	0.0192	0.0099

It can be seen from the results in Table I that, as expected, the internal water constitutes the greatest percentage of the total for the sugar of greatest mean aperture. The internal water varies from 46 to 85 per cent. of the total.

#### COMPARISON WITH THE STANDARD METHOD

A recommendation of the International Commission for Uniform Methods of Sugar Analysis<sup>5</sup> states that water in granulated sugar should be determined by measuring the loss in weight on heating at 105° C for 3 hours. At the laboratories of Tate & Lyle Ltd., the heating period is 1 hour. A comparison of the 1-hour procedure with the proposed method, with and without grinding, was made. The average of ten determinations by the proposed method with grinding was 0.0414 per cent. of water, the average of two determinations by the proposed method without grinding was 0.0136 per cent. and the average of two determinations by the standard method was 0.012 per cent. Within the limits of error, the standard method gives a reasonably accurate figure for the external water.

#### COMPARISON WITH THE METHOD OF GARDINER AND KEYTE

The results of determinations on four types of sugar by the proposed method and by the method of Gardiner and Keyte,<sup>3</sup> which is based on a reaction with cobaltous bromide, were as follows—

	Granulated sugar	Powdered sucrose	Sucrose crystals	Refined sugar No. 3
Water found by cobaltous bromide method, %	0.047	0.013	0.018	0.066
Water found by proposed method, %	0.0414	0.0132	0.0195	0.0395

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# A Study of Some Methods for Determining Water in Refined Sugars, Including the Newly Devised Cobaltous Bromide Method

BY S. D. GARDINER AND H. J. KEYTE

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The adsorption of cobaltous bromide reagent solution by refined sugar crystals, with and without grinding, is used as a method of determining total water and surface water, respectively. Comparison is made with water determined by oven-drying methods and a vacuum-distillation method.

TOTAL water in the sugar crystal may be considered to include (a) free water, called moisture, that is readily driven off by normal methods of drying in an oven, and (b) water bonded to the crystal structure, which is released only after very fine grinding. Syrup is known to be entrapped during the physical build up of the crystal. This "building in" of syrup, *i.e.*, water, has been reported by Powers,<sup>1</sup> and illustrated by his descriptive photomicrographs and electron micrographs.

The normally accepted method for determining moisture in pure sucrose and refined sugars is by drying in an oven at 105° C for  $\frac{1}{2}$  hour,<sup>2</sup> and the results are used as a guide to the true water content of the crystal. When pure sucrose crystals are used as a primary analytical standard, *i.e.*, for polarimetry, it is usual to grind the crystals carefully before drying to a specific surface of approximately 3500 sq. cm per g, so that total water is exposed. The true water content of the crystals is not required, but only that which remains, so that a correction can be made to the weight of powdered sucrose used for calibration purposes. During grinding water may be lost or gained. Normal drying methods based on the measurement of percentage loss of weight have three serious disadvantages, namely, (a) incomplete cooling due to inefficient desiccator design, (b) the formation of degradation products due to heat, and (c) inability to measure total water content. These can be overcome, first by cooling for a long time or by using a water-cooled copper block in the desiccator, secondly by preparing a graph of percentage loss of weight against time of drying and applying a correction for destruction<sup>3</sup> and thirdly by grinding the crystals under specific conditions before heating. A method in which heat is not used is advantageous.

Two newly devised chemical methods are described, in which cobaltous bromide dissolved in dry chloroform, a reagent that has very great affinity for water, is used. They are (a) chloroform extraction method using cobaltous bromide reagent, (b) cobaltous bromide reagent adsorption method. The first is only very briefly described because chloroform extracts only "free" or surface moisture from refined sugar crystals, ground or unground, and therefore is no better than the normal conventional methods already in use. In the second method, the forces retaining water in the crystal structure are overcome by allowing the cobaltous bromide reagent to react with this water *in situ*, *i.e.*, after adsorption by the crushed crystals; it has revealed a water content greater than was expected.

Briefly described, chloroform is used in the first method to extract water from the crushed crystals during the grinding process in a ball mill, and, after separation, the "wet" chloroform is treated under dry air conditions with cobaltous bromide reagent to precipitate the water as a cobaltous bromide hydrate (or complex). The precipitate is washed, dried and weighed as anhydrous cobaltous bromide. Standardisation of the method is by determining added water. The results given in Table I, p. 153, show that the water extracted by chloroform is surface moisture. The second method is described below.

## METHOD FOR THE DETERMINATION OF WATER IN REFINED SUGARS BY ADSORPTION OF COBALTOUS BROMIDE REAGENT ON THE GROUND SUGAR

### APPARATUS—

Fig. 1 shows the two-piece grinding and filtration apparatus and one of four "pipette flasks." The grinding vessel is 4 inches in diameter and holds six  $\frac{3}{4}$ -inch diameter stainless-steel balls. The top filtration section is fitted with a No. 2 sintered-glass filter disc.

The B29 joint must be fitted with a sleeve. The rubber bung and polythene disc, 4 inches in diameter, fit over the top part to support the apparatus and to facilitate rotation on rollers during grinding. The rubber covered rollers are  $1\frac{1}{2}$  inches in diameter and are spaced  $3\frac{3}{4}$  inches apart between centres; they are inclined at  $20^\circ$  to the horizontal and rotate at 160 r.p.m.

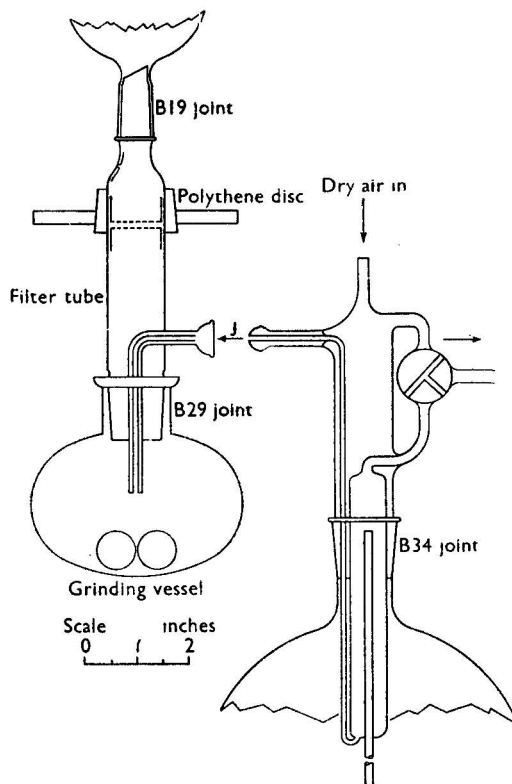


Fig. 1. Apparatus for determining water by the cobaltous bromide method

There are four pipette flasks and one is seen on the right-hand side of Fig. 1. One delivers 5 ml of dry chloroform, the second 5 ml of standard "wet" chloroform, the third 20 ml of cobaltous bromide reagent dissolved in chloroform and the fourth 12.5 ml of dry carbon tetrachloride. The last reagent is kept in contact with anhydrous cobaltous bromide. This flask is fitted with a medium-porosity glass sinter to separate the liquid from the solid. Volumes are delivered to within  $\pm 0.1$  ml. The pipette section of the flask is filled automatically by blowing dry air through the top of the apparatus, and later, by manipulation of the three-way stopcock, the specified amount of reagent is blown into the grinding vessel, which is attached in readiness at the spherical joint, J. Strict precautions are taken at all times to prevent ingress of moist air. Caps are used to seal joint J when it is not in use. Glassware is dried at  $105^\circ$  C overnight, except the grinding vessel, which, because of its thickness, is dried by using absolute ethanol. The apparatus is flushed out with dry chloroform before use.

#### REAGENTS—

*Cobaltous bromide reagent solution*—A solution of recrystallised cobaltous bromide in chloroform, containing 150 mg of cobaltous bromide per 20 ml.

*Carbon tetrachloride*—Analytical-reagent grade.

*Chloroform*—Analytical-reagent grade.

*Standard "wet" chloroform*—Chloroform containing 5 mg of water per 5 ml.

These reagents are stable. Recrystallised cobaltous bromide is obtained directly from the manufacturer. The crystals are partly dried in a mortar at  $105^\circ \pm 1^\circ$  C for a few hours

and the bluish product is ground to facilitate complete dehydration on further heating. The finely powdered cobaltous bromide keeps excellently in its anhydrous state and is conveniently stored in an oven at  $105^{\circ}\text{C}$ . The dark-magenta hydrated crystals are pale green when anhydrous and are extremely hygroscopic. Because of the hygroscopicity, the cobaltous bromide reagent solution is prepared from an approximately saturated solution of the salt (1.1 per cent. w/v) in chloroform at room temperature. As the concentration of the saturated solution can be determined (see below, "Determination of cobaltous bromide in the filtrate"), the cobaltous bromide reagent solution is prepared by proportional dilution with chloroform. The reagent solution is kept in the presence of dry air; its strength will decrease slowly with time, owing to the inevitable pick-up of water from the air and the subsequent precipitation of a few reddish crystals of hydrated cobaltous bromide. Re-determination is needed every few days; a variation of  $\pm 10$  mg of cobaltous bromide per 20 ml will not seriously affect the slopes of the calibration curves for water described later. The reagent solution is checked by drying an aliquot overnight at  $105^{\circ} \pm 1^{\circ}\text{C}$  and weighing the residue as cobaltous bromide,  $\text{CoBr}_2$ . Chloroform can be obtained with very little contamination from water, if any, and blank tests can be made to determine these unknown amounts. Cobaltous bromide was tested for metallic impurities by Gross,<sup>4</sup> who used his high-voltage electrophoresis technique, and showed that the reagent was free from nickel, iron, copper, manganese and lead. The standard "wet" chloroform is prepared by adding water from an Agla micrometer-syringe pipette to a known amount of analytical-reagent grade chloroform. Carbon tetrachloride, which normally contains some water, is dried by the addition of freshly dried cobaltous bromide powder, excess of which remains in the flask.

#### PROCEDURE FOR PREPARING THE CALIBRATION GRAPH FOR TOTAL WATER—

*Initial preparation of powdered sucrose*—The six stainless-steel balls are placed in the grinding vessel and  $30 \pm 0.5$  g of sucrose crystals are ground for 30 minutes  $\pm 10$  seconds in the presence of  $32.5 \pm 0.5$  ml of undried carbon tetrachloride. The powder is separated by filtration using dry air technique to prevent condensation of moisture and agglomeration of particles, and partly dried at  $105^{\circ}\text{C}$  for 15 minutes.

*Drying the powdered sucrose*—The powdered sucrose is dried immediately before a test point on the curve is required. The aim is to dry the powder irrespective of the slight formation of degradation products. It is dried at  $105^{\circ} \pm 1^{\circ}\text{C}$  for 2 hours in a flat-bottomed metal dish that has a spout at one end, so that when dry the hot powder can be quickly transferred to the grinding vessel and allowed to cool under dry air conditions. Dry air is used to expel moist air when required.

*Procedure*—Cobaltous bromide is adsorbed by the exposed active surfaces of the dry ground sucrose crystals. A blank test determines this amount together with the cobaltous bromide removed by traces of water in the chloroform, ingress of moist air, etc. Points on the calibration graph for total water (curve B, Fig. 2) are determined by the procedure described below, excluding the initial grinding phase, and substituting standard "wet" chloroform for dry chloroform. In this way, cobaltous bromide removed is correlated with milligrams of water in the presence of dry sucrose powder.

#### PROCEDURE FOR DETERMINING TOTAL WATER IN REFINED SUGARS—

*Initial grinding*—Four 5-ml portions of chloroform, 12.5 ml of carbon tetrachloride and  $30 \pm 0.5$  g of refined sugar crystals are transferred to the dry grinding vessel. The polythene disc is placed in position and the flask is rotated for 30 minutes  $\pm 10$  seconds. Large crystals may need longer time and very small crystals less time. The criterion is a specific surface of  $3500 \pm 200$  sq. cm per g.

*Addition of cobaltous bromide reagent solution*—The grinding assembly is removed from the rollers and 20 ml of the cobaltous bromide reagent solution of previously determined concentration are added. The flask is rotated for a further 10 minutes  $\pm 10$  seconds. During this period, the reagent is given ample time to react with the bonded water exposed by grinding and there is a slight increase in specific surface. Immediately the second grinding phase is over, the remaining cobaltous bromide is filtered into the top flask by inverting the assembly and applying a pressure of dry air of 2 to 4 lb per sq. inch to speed up filtration.

*Determination of cobaltous bromide in the filtrate*—A 10-ml aliquot is heated at  $65^{\circ}$  to  $70^{\circ}\text{C}$  to volatilise the chloroform and carbon tetrachloride and dried at  $105^{\circ} \pm 1^{\circ}\text{C}$  for 2 hours,

or overnight, to produce anhydrous cobaltous bromide, which is weighed when cold. A circular silica capsule with ground lid<sup>5</sup> is used.

CALCULATION OF RESULTS—

Amount of cobaltous bromide added to test .. = 150 mg  
 Volume of solution .. .. . = 52.5 ml  
 Amount of cobaltous bromide in 10 ml of filtrate .. =  $W$  mg  
 Therefore amount of cobaltous bromide in 52.5 ml =  $W \frac{52.5}{10}$  mg

Therefore amount of cobaltous bromide removed .. =  $150 - W \frac{52.5}{10}$  mg

This result, when referred to the calibration curve for total water (curve B, Fig. 2) gives the result for the total water in 30 g of refined sugar.

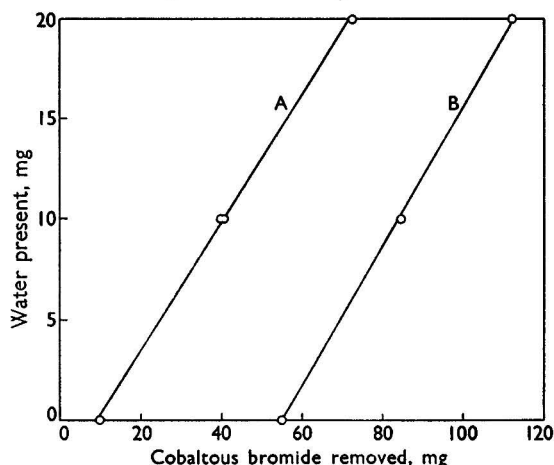


Fig. 2. Calibration curves: curve A, surface moisture; curve B, total water

PROCEDURE FOR DETERMINING SURFACE MOISTURE IN REFINED SUGARS—

Determinations are carried out in a similar way to the total-water determinations, except that the initial grinding period of 30 minutes is omitted, and the six stainless-steel balls are not present during the 10 minutes' mixing with the cobaltous bromide reagent solution. A calibration graph for surface moisture (curve A, Fig. 2) is prepared in a similar manner to the calibration graph for total water.

TABLE I  
 DETERMINATION OF WATER IN REFINED SUGARS

Sample	Water found by drying in an oven at 105° C for—		Water found by drying in a vacuum oven at 70° C for 20 hours, %	Water found by adsorption on cobaltous bromide method—		Water found by chloroform extraction of cobaltous bromide reagent with grinding, %	Water found by vacuum distillation with grinding,* %
	1 hour, %	3 hours, %		without grinding, %	with grinding, %		
	Refined sugar No. 1 ..	0.011		0.012	—		
Refined sugar No. 2 ..	0.012	0.017	—	0.013	0.047	—	0.0414
Powdered sucrose ..	0.008	0.017	0.016	—	0.013	0.006	0.0132
Sucrose crystals ..	0.002	0.003	0.003	<0.002	0.018	0.006	0.0195
Refined sugar No. 3 ..	0.026	0.039	0.016	0.012, 0.014	0.066, 0.055, 0.056	—	0.0395

\* Results supplied by S. Hill and A. G. R. Dobbs.\*

Table I gives the results of determinations of water in refined sugars and sucrose by several methods. Comparison is made to show that serious differences exist, and that revision, or possibly rejection, of normally accepted methods is to be advocated.

#### DISCUSSION OF RESULTS

Heat, whether by thermal conduction or radiation (by infra-red rays) or heated air, causes degradation products, which interfere with the determination of water.

Table II shows the high results produced by incomplete cooling of one aluminium dish with lid and 20 g of refined sugar, which indicate that drying in an oven is not suitable as a routine method for the determination of moisture.

TABLE II

#### HIGH RESULTS CAUSED BY INCOMPLETE COOLING IN THE DETERMINATION OF MOISTURE BY DRYING IN AN OVEN

Water was determined by heating for 1 hour at 105° C

Sample	Water found after cooling for 20 minutes in—		Water found after cooling for 90 minutes in—	
	No. 1* desiccator, %	No. 2† desiccator, %	No. 1* desiccator, %	No. 2† desiccator, %
Sucrose finely ground ..	0.028	0.013	0.009	0.009
Sucrose crystals ..	0.025	0.002	0.002	0.001
Caster sugar ..	0.029	0.012	0.016	0.011
Refined sugar ..	0.032	0.014	0.016	0.014

\* Containing barium oxide.

† Containing barium oxide and a water-cooled copper block, the cooling water being at the balance temperature.

Table I shows that, for accurate water determinations, sugar crystals must be ground to a specific surface of 3500 sq. cm per g to expose all the bonded water. In the cobaltous bromide method the increase of invert sugar is less than 0.005 per cent. Dry methods of grinding can cause serious local increase of temperature at the many points of contact, and also greater formation of invert sugar.

The determination of water in sugar crystals by drying in a vacuum oven at 70° C is satisfactory in that the results agree well with surface-moisture determinations by the cobaltous bromide method (see curve A, Fig. 2). Drying in an oven at 105° C for 1 hour gives a higher result for surface moisture because of partial decomposition and possible breakdown of the sugar crystal by excessive heat. Further experiments, in which the crystals were dissolved in distilled water and dried on Celite powder, were tried exhaustively, but the results were erratic. The very small losses in weight made the method too difficult.

#### CONCLUSIONS

There is no doubt that, as suggested by Powers, the sugar crystal conceals more internal water than is generally assumed. The water can be measured by the adsorption of cobaltous bromide reagent on the ground crystal, provided the specific surface is at least 3500 sq. cm per g, and this is considered to be suitable as a routine method for total water. Surface moisture can also be speedily determined. The cobaltous bromide method is not absolute, as it requires standardisation by water in the presence of dry sucrose powder of specific surface of 3500 sq. cm per g.

The adsorption on cobaltous bromide method may be simplified by using only the first and third reagents. A slight loss of sensitivity is caused by not using carbon tetrachloride. Instead of the use of "wet" chloroform, water is added directly to the grinding vessel from an Agla micrometer-syringe pipette. The few drops of water are added through the side-arm and washed down by chloroform and cobaltous bromide reagent solution. Time is reduced considerably if the gravimetric method for the determination of cobaltous bromide is replaced by a comparative electrical conductivity method.

We express our thanks to the Directors of Tate & Lyle Limited for permission to publish this work, and to D. Buxton for the many pieces of glass apparatus made by him. We also thank F. J. Gardiner (*née* F. J. Farmiloe) and R. Runeckles for their co-operation.

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## The Determination of Monobromamine and Monochloramine in Water

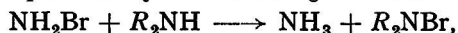
By J. K. JOHANNESSON

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Chlorination of waters containing both bromide and ammonia, such as obtains in sea-water swimming pools, leads to the formation of both monochloramine and monobromamine. The amount of these substances present may be determined (a) by reaction of the monobromamine with neutral *o*-tolidine and titration with ammonium ferrous sulphate—addition of potassium iodide then permits the determination of monochloramine—and (b) in neutral solution at zero applied voltage, monobromamine alone is titrated at the rotating platinum electrode with phenyl arsenoxide. Monochloramine is then determined by addition of potassium iodide and further titration with the same reagent.

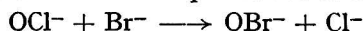
It was shown by Johannesson in a previous publication<sup>1</sup> that, when chlorine is added to a solution containing excess of bromide together with ammonia, either monobromamine or monochloramine, or both, are formed according to the reaction conditions. When the chlorine is added in neutralised form, *i.e.*, as sodium hypochlorite, to alkaline solutions at pH 8.0 containing an excess of bromide and ammonium ions, only monochloramine is formed. Conversely, under acid conditions of reaction for both reactants, only monobromamine is formed. Addition of an acid solution of chlorine to excess of bromide and ammonium ions, in a solution containing a reserve of alkalinity, such that the final mixture is not acid, results in a mixture of the amines, the proportion of each present depending upon, among other factors, the rate of mixing, *i.e.*, formation of local acidity.

Previously, Houghton<sup>2</sup> had made some investigations on the chlorination of water containing bromide and showed that there was some evidence of the formation of monobromamine in the presence of ammonia, but he was uncertain as to what actually existed in the solutions. He further found that solutions containing an excess of bromide and ammonia were, when chlorinated, more bactericidal than pure monochloramine solutions. I have found that solutions of monobromamine are much more strongly bactericidal than monochloramine solutions of the same equivalent oxidising strength and, further, that the bactericidal effects are complicated by the following reaction—

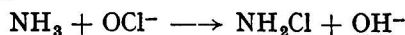


the  $\text{R}_2\text{NH}$  arising by diffusion from the bacterial cells. This type of reaction has been demonstrated with dimethylamine in amperometric titration apparatus. This effect is shown by the break in the curve when the logarithm of the number of survivors is plotted against time. As can be seen from Fig. 1, no such effect is observed with monochloramine.

Farkas and Lewin<sup>3</sup> have shown that at pH values of 10 to 12 the reaction—



is very slow and not complete even after many hours; at pH 8 to 10 the reaction is still slow and requires some minutes for completion. Only below pH 8 is the reaction rapid. On the other hand, the reaction—



is one of the most rapid reactions known. Laitinen and Woerner<sup>4</sup> titrated ammonia amperometrically with hypochlorite in the presence of bromide at pH 8.2 and presumably the excess

of hypochlorite over that required to form monochloramine reacts with the bromide to give hypobromite, which will react in turn with the monochloramine and cause a rapid over-all decomposition.

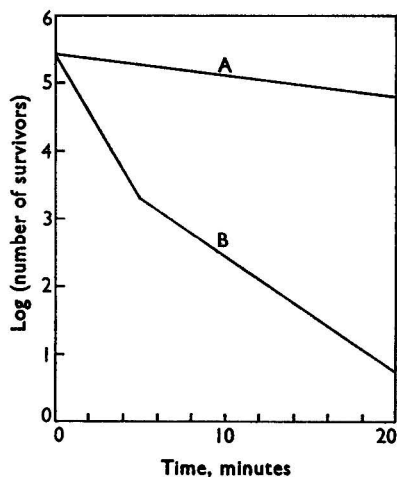


Fig. 1. Death rate of *Escherichia coli* in the presence of  $10^{-3}$  M ammonium sulphate at pH 8.2 with sodium hydrogen carbonate buffer solution at  $15^{\circ}$  C on exposure to: curve A, monochloramine; curve B, monobromamine. The concentration of each bactericide was 0.15 p.p.m., as chlorine

The chlorination of sea-water swimming pools containing ammonia from the bathing load or of sea water containing sewage usually involves the addition of a solution of free chlorine, which gives rise to both monochloramine and monobromamine.

The study and control of the chlorination in these circumstances requires the use of methods of analysis that will differentiate between monochloramine and monobromamine.

Although a spectrophotometric method permits the determinations to be made when the chlorine dose is about 10 p.p.m. or higher, the residuals encountered in practice are usually between 0.2 and 0.8 p.p.m., expressed as chlorine, and require the use of much more sensitive methods of determination.

TABLE I

EFFECT OF MONOBROMAMINE AND MONOCHLORAMINE ON VARIOUS METHODS OF DETERMINING RESIDUALS

Method	Remarks
Potassium iodide with starch as indicator in—	
(a) acid solution .. .. .	Monobromamine and monochloramine react
(b) neutral solution .. .. .	Monobromamine and monochloramine react
<i>o</i> -Tolidine in—	
(a) acid solution .. .. .	Monobromamine and monochloramine react
(b) neutral solution .. .. .	Monobromamine only reacts
Methyl orange in acid solution .. .. .	Monobromamine only reacts
Amperometric at 0.2 volt measured against the saturated-calomel electrode (pH 7.2) ..	Monobromamine only reacts

When bromide is present, free chlorine and halogen amines can have only a momentary co-existence. A method mentioned later (see p. 157) for the determination of monobromamine and monochloramine, *i.e.*, the F.A.S. method, will not differentiate between free bromine, combined bromine and free chlorine. The proposed method, amperometric titration, will, however, permit this distinction to be made.



SURVEY OF POSSIBLE METHODS FOR DIFFERENTIATING BETWEEN  
MONOBROMAMINE AND MONOCHLORAMINE

Solutions of monobromamine were prepared by adding freshly prepared bromine water to 0.1 *M* ammonium sulphate containing 300 p.p.m. of sodium hydrogen carbonate. Monochloramine was similarly prepared, but with chlorine water instead of bromine water. The concentrations were made to about 1.0 p.p.m., expressed as chlorine.

The solutions were tested by using the usual methods and reagents for determining chlorine, and the results of these tests are given in Table I. Three of the methods appeared to be suitable and they were examined in greater detail; they were the methyl orange, the neutral *o*-tolidine and the amperometric titration methods.

METHYL ORANGE METHOD—

Methyl orange was introduced by Taras<sup>5</sup> for determining free chlorine. At pH 3 or less, it reacts instantaneously with free chlorine, but not with monochloramine. At this pH, monobromamine reacts rapidly, apparently owing to appreciable hydrolysis, as follows—



However, in the presence of bromide at pH 3, monochloramine reacts rapidly with methyl orange and so renders this method impracticable for the purpose of this investigation. Methyl red behaves similarly.

*o*-TOLIDINE METHOD—

With an acidified solution of *o*-tolidine, both monochloramine and monobromamine react, the latter rapidly. Palin<sup>6</sup> introduced a neutral *o*-tolidine reagent mixed with sodium hexametaphosphate to act as a combined buffer and sequestering agent. This reagent forms a blue quinonoid compound with free chlorine, but does not react with monochloramine. The blue colour can be determined colorimetrically or, better, titrated with ammonium ferrous sulphate to the disappearance of the colour. At this stage, addition of iodide causes any monochloramine that may be present to react, producing a further blue compound, which can then be titrated with ammonium ferrous sulphate.

As it was found that monobromamine behaves with this reagent as if it were free chlorine and, further, that monochloramine in the presence of bromide does not react, it was possible to evolve a suitable method for the determination of the concentration of both monochloramine and monobromamine when they are present together.

It was found that the F.A.S. method, as described by Palin,<sup>7</sup> would differentiate between monobromamine and monochloramine, the monobromamine reacting as if it were free chlorine. Free bromine will, of course, also react as if it were free chlorine and consequently the method will not distinguish between these forms, but, after an excess of an ammonium salt has been added, chlorine will no longer react.

This method is not, however, suitable for use with sea water, as the phosphate buffer solutions cause precipitation of the magnesium salts and the resulting turbidity interferes with the titration.

It is convenient to express all results in parts per million, as "chlorine."

$$\text{"Chlorine" present} \equiv \frac{\text{titre, ml} \times \text{volume of test solution, ml}}{100} \text{ p.p.m.,}$$

where 1 ml of standard ammonium ferrous sulphate solution  $\equiv$  0.1 mg of chlorine.

AMPEROMETRIC METHOD—

The initial experiments were made with a large-area rotating electrode, which was made by coating a glass bulb at the end of a hollow glass rotor with a conducting film of platinum deposited by applications of saturated platinum chloride solution and heating. Electrical contact was established by means of a platinum wire sealed through the glass. This has been described elsewhere.<sup>8</sup> At a later date, a Wallace and Tiernan apparatus became available.

Marks and Bannister<sup>9</sup> found that at neutral pH values the chlorine wave commenced near +0.7 volt measured against the saturated-calomel electrode, the monochloramine wave being much more negative. Further, at these pH values sodium arsenite and phenyl arsenoxide reduce only free chlorine, but, when iodide is added, the monochloramine liberates

free iodine, which yields a reduction wave and at this applied potential is also reduced by the above-mentioned reagents.

I have found that the monobromamine wave commences at approximately +0.5 volt measured against the saturated-calomel electrode and that it is reducible with both arsenite and phenyl arsenoxide. It was therefore possible to use this method for the determination of monobromamine and, further, by adding iodide, to determine monochloramine when present at the same time.

In the presence of sodium hexametaphosphate it is possible to titrate the monobromamine with ammonium ferrous sulphate, but the rate of reaction is somewhat slow and, further, the graph of the volume of titrant against current is not linear, as it is when the arsenic compounds are used. Titration with phenyl arsenoxide is recommended.

As mentioned previously, free chlorine will not co-exist, other than momentarily, with the halogen amines when bromide is present, nor will bromine in the presence of monobromamine or monochloramine. If free bromine or chlorine is present, addition of an ammonium salt will cause a large and rapid decrease of diffusion current to a quarter or less of the original value. If there is no reduction of current, then the combined forms are present and of these only monobromamine will be titrated with phenyl arsenoxide. Subsequent addition of potassium iodide permits the monochloramine to be titrated.

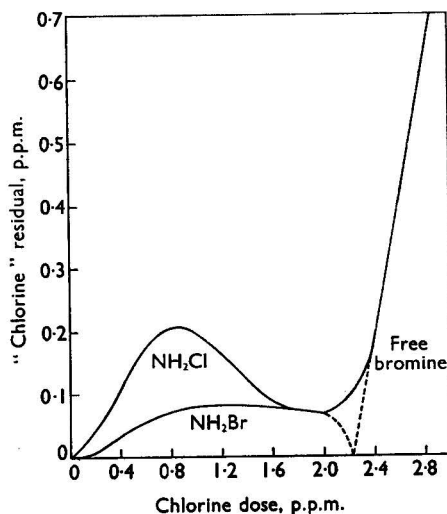


Fig. 2. Chlorination of sea water, containing natural bromide with 0.26 p.p.m. of ammonia added, by treating it with increasing amounts of sodium hypochlorite and then determining the nature of the residue after 30 minutes

#### METHOD

##### REAGENTS—

*Phenyl arsenoxide solution*—Dissolve 0.4 g of phenyl arsenoxide<sup>10</sup> in a small amount of dilute alkali solution, dilute to nearly 1 litre with distilled water and adjust the pH to between 6 and 7 with dilute hydrochloric acid. Standardise against standard iodine, using starch as indicator.

1 ml  $\equiv$  (factor from standardisation)  $\times$  0.2 mg of chlorine.

*Sodium hydrogen carbonate*—Analytical-reagent grade.

*Ammonium sulphate solution*, N.

*Potassium iodide solution*, 1 per cent. aqueous.

##### PROCEDURE—

With the amperometric titration apparatus set at zero applied volts, 200 ml of the test solution are placed in the apparatus and approximately 0.2 g of sodium hydrogen carbonate

is added. The current reading is observed and then 1 ml of ammonium sulphate solution is added. A large reduction of current indicates that free bromine or chlorine is present, and no reduction of current indicates that the combined forms are present.

The solution is now titrated with the phenyl arsenoxide solution until no further change of current occurs. This titration represents either bromine or monobromamine, according to whether free or combined bromine is present.

One millilitre of potassium iodide solution is now added and the titration is continued until once again there is no further reduction of current. This additional titration represents either chlorine or monochloramine, according to whether free or combined chlorine is present.

As mentioned before, it is convenient to calculate the results as p.p.m. of chlorine.

Chlorine, p.p.m. = volume of phenyl arsenoxide solution used, ml.

## RESULTS

Table II shows a comparison between results by the F.A.S. method and the proposed method. Fig. 2 shows the results obtained from the chlorination of sea water containing an excess of ammonia, the determinations being made by the amperometric method.

TABLE II

### COMPARISON OF RESULTS BY DIFFERENT METHODS

The test solutions were prepared as described on p. 157

Found by F.A.S. method			Found by amperometric method		
Monobromamine, as chlorine, p.p.m.	Monochloramine, as chlorine, p.p.m.	Total, as chlorine, p.p.m.	Monobromamine, as chlorine, p.p.m.	Monochloramine, as chlorine, p.p.m.	Total, as chlorine, p.p.m.
0.95	1.00	1.95	0.93	0.95	1.88
0.65	0.65	1.30	0.64	0.68	1.32
0.63	0.50	1.13	0.65	0.45	1.10
0.35	Nil	0.35	0.41	Nil	0.41
0.50	Nil	0.50	0.49	Nil	0.49
Nil	0.72	0.72	Nil	0.72	0.72
0.30	0.65	0.95	0.25	0.69	0.94

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## Determination of Free Lime in Lime and Silicate Products

### Part I. Extraction of Freshly Ignited Lime with Non-aqueous Solvents and Determination of the Calcium Oxide Content of the Extracts

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An examination of methods of extracting calcium oxide from freshly ignited lime by various non-aqueous extracting agents and its determination by potentiometric, volumetric and complexometric methods has been carried out. New indicators have been recommended for the visual alkalimetric titration of the extracts. The use of these indicators gives values consistent with those obtained by potentiometric titrations.

Various factors, such as the ratio of the extractant to alcohol in the titration medium, the percentage of water that can be tolerated therein and the possibility of using industrial methylated spirit, have been examined. These factors can be a source of error in such determinations.

DETERMINATION of "free lime" in lime and silicate products, such as cements, pozzolanas, mortars and concrete, is very often required in the evaluation of these materials. In the past, many methods have been developed and have also been critically examined for their accuracy. The chemical methods for the determination of "free lime" involve essentially the extraction of "free lime" by aqueous or non-aqueous solvents and then the determination of the calcium oxide content of the extract by a suitable titration method.

Several aqueous solvents, such as lime water,<sup>1</sup> dilute and weak acids, solutions of an ammonium salt<sup>2</sup> and sugar,<sup>3</sup> have been used. As with these extracting agents there is a likelihood of increase in the extracted calcium oxide content caused by hydrolysis of the silicate,<sup>4</sup> the use of non-aqueous solvents has been preferred to that of aqueous solvents.

Of the several non-aqueous extracting agents, glycerol was suggested by Emley<sup>5</sup> and its use was re-examined by a number of workers. The extracted lime was titrated against ammonium acetate by Lerch and Bogue,<sup>6</sup> against benzoic acid by Bessey<sup>7</sup> and against tartaric acid by Rathke.<sup>8</sup> Konarzewski and Lukaszweics<sup>9</sup> used phenol for extracting lime and titrated the extract with standard hydrochloric acid. The method was extended to pozzolanic mixtures by Sestini and Santarelli<sup>9</sup> and by Wittekindt.<sup>10</sup> Schläpfer and Bukowski<sup>11,12</sup> used ethylene glycol for extracting lime, and this method has been extended to hydrated cement mixes by Forsen<sup>13</sup> and Rødt,<sup>14</sup> and to clinkers and Portland cements by MacPherson and Forbrick.<sup>15</sup> The Associated Cement Company of India<sup>16</sup> also use ethylene glycol for extracting "free lime" from cement. Franke<sup>17,18</sup> used a mixture of acetoacetic ester and *isobutyl* alcohol for extracting "free lime" from cements.

Assarsson and Bokström<sup>19</sup> separated the free calcium oxide in lime and silicate products by using some of the previously mentioned extracting agents and carried out the determination by titrating the extract against standard hydrochloric acid or benzoic acid. For visual titrations these investigators used the same indicators as previous workers. They also carried out potentiometric and conductimetric titrations on the extracts. On analysis of their results, it appears that, although the method suggested—titration of the extracted calcium oxide with a strong acid—is an improvement over the earlier method of titration with ammonium acetate, the results when different indicators are used are unreliable and there is no correlation between the results by visual and potentiometric titrations. From the original paper of Konarzewski and Lukaszweics<sup>9</sup> it was noted that the factor used by them for the calcium oxide determination is arbitrary. Normally, 1 ml of *N*/15 hydrochloric acid should be equivalent to 0.00187 g of calcium oxide, whereas these authors found that it is equal to 0.00202 g. Similarly, when reference was made to the work of MacPherson and Forbrick<sup>15</sup> on the determination of "free lime" in cements, it was noted that a rather unconventional procedure was adopted. Pre-treatment of the solvent, *viz.*, ethylene glycol, was carried out with calcium oxide and it was then titrated against an acid, a mixture of phenolphthalein and naphtholphthalein being used as the indicator; the pre-treated ethylene glycol

was used for extracting calcium oxide from cement, the titration again being carried out in the same manner.

In a paper presented at the symposium on the Chemistry of Cements held at Stockholm in 1938, Bessey<sup>4</sup> drew attention to the views held by various authors on the inadequacy of reliable procedures for assessing the accuracy of "free lime" determinations, and the position does not seem to have improved since.

In our view, an important point that requires consideration in calcium oxide - acid titrations is the choice of indicators. It is well known that both the sensitivity and pH range of response of indicators in non-aqueous media are not<sup>20,21</sup> necessarily the same as in aqueous media. This fact seems to have been largely overlooked by the previous investigators.

In view of these facts and also the lack of a well defined and agreed procedure of extraction, the uncertainty of conversion factors and the use of indicators that may not be suitable for titration in non-aqueous media, it was considered desirable to re-investigate the problem.\* Particular care was taken during the study of the various factors involved in the extraction of calcium oxide from freshly ignited lime and its determination by electrometric and ordinary volumetric titrations. Recently developed complexometric titration procedures were also used in these determinations, and it is hoped that applications of these procedures to the investigation of lime and silicate products will be discussed in a separate paper. The method of Emley and of Lerch and Bogue—titration of the extract with ammonium acetate—was not used, as it was too time-consuming.

#### EXPERIMENTAL

The experimental work was divided into the following steps—

- (i) Procedure for extracting calcium oxide from freshly ignited lime with various non-aqueous solvents, *viz.*, glycerol, ethylene glycol and phenol, and also the procedure for diluting the extracts to standard volumes.
- (ii) Plotting of potentiometric titration curves of these extracts by titrating with standard hydrochloric acid and determining the titre from the maximum  $d(\text{pH})/dv$  value.
- (iii) Determination of the extracted calcium oxide by titrating with hydrochloric acid, use being made of both the established and the newer indicators.
- (iv) Complexometric titration of the extracts from lime.
- (v) A study of the effect of adding ethanol or water, or ethanol *plus* water, to the calcium oxide extracts on the shift of end-point in potentiometric determination and the change in titre when visual indicators are used.
- (vi) Practicability of the use of distilled rectified spirit or industrial methylated spirit (without drying) for the final dilution of the extracts.

#### APPARATUS AND REAGENTS—

A Beckman pH meter, model H2, with glass calomel electrodes was used for the potentiometric titrations.

The reagents used in the experimental work were as follows—

*Calcium oxide*—This was prepared by fully igniting AnalaR calcium carbonate at 850° to 900° C for 2 hours. The loss on ignition for different batches varied from 43.5 to 43.9 per cent.

*Glycerol*—The B.P. grade was further purified by collecting the fraction boiling at 177° to 178° C under a pressure of 7 to 8 mm of mercury.

*Ethylene glycol*—The C.P. grade was further purified by distillation, and the fraction boiling at 195° C was collected.

*Phenol*—The C.P. grade was further purified by distillation, and the fraction boiling between 178° and 180° C was collected.

*Ethanol*—Rectified spirit was purified by distillation over lime and finally by treatment with anhydrous copper sulphate. The distillate when tested was free from water, lime, copper and so on, and was neutralised, when necessary, before it was used for dilution purposes.

*Water, double-distilled*—Free from calcium ions.

*Ethanolic hydrochloric acid*—An approximately 0.05 N solution.

1 ml  $\approx$  1.4 mg of calcium oxide.

\* Since the preparation of this paper, Pressler, Brunauer and Kantro<sup>22</sup> have investigated Franke's method of extraction with acetoacetic ester.

*Ethanolic sulphuric acid*—An approximately 0.05 *N* solution.

*Methyl orange indicator solution*—A 0.1 per cent. aqueous solution.

*Mixed methyl red - methylene blue indicator solution*—A solution containing 0.1 per cent. of each.

*Alizarin S indicator solution*—A 0.1 per cent. aqueous solution.

*Bromocresol green indicator solution*—A solution obtained from the British Drug Houses Limited was used.

*Disodium ethylenediaminetetra-acetate solution*—An aqueous solution standardised against the standard calcium solution.

*Standard calcium solution*—A known amount of dried AnalaR calcium carbonate was dissolved in hydrochloric acid and diluted to a definite volume.

*Ammonium chloride - ammonium hydroxide buffer solution*—This was prepared by dissolving 67.5 g of ammonium chloride in 570 ml of ammonia solution, sp.gr. 0.880, and diluting to 1 litre.

*Eriochrome black T indicator solution*—A 1 per cent. solution in ethanol.

#### EXPERIMENTS WITH GLYCEROL AS THE EXTRACTING AGENT—

*Preparation of solution of calcium oxide in glycerol*—A known weight of freshly ignited lime (0.05 to 0.200 g) was transferred rapidly to a conical flask fitted with a B24 ground-glass joint and containing about 10 ml of anhydrous glycerol; 40 ml of anhydrous glycerol were added and the flask was stoppered and set aside overnight. At the end of this period, a condenser having a calcium chloride tube at its other end was fitted to the flask. The flask was heated on a water bath for 6 to 9 hours. During the heating, any speck of undissolved lime was broken with a glass rod. The solution was heated until clear. This solution was cooled and diluted to a known volume (250 or 500 ml) with dried neutralised ethanol. The possibility of water entering the extracting solvent during dissolution of the lime was reduced by using a reflux flask fitted with the cone of a standard joint, the condenser being fitted with the socket of the joint.

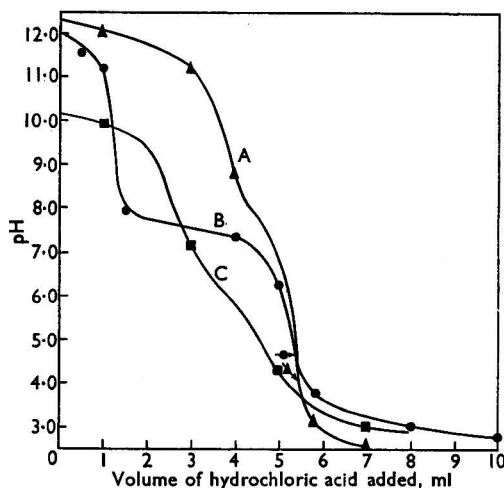


Fig. 1. Titration of calcium oxide extracted with glycerol: curve A, extract with ratio of ethanol to glycerol of 4 to 1; curve B, extract with ratio of ethanol to glycerol of 50 to 1; curve C, extract with ratio of ethanol to glycerol of 4 to 1, containing 85 per cent. of water. The arrows correspond to the points at which  $\frac{d(\text{pH})}{dv}$  are maxima

*Potentiometric titration*—Aliquots of the prepared solution (generally 25 ml) were diluted with different amounts of purified anhydrous ethanol and potentiometric titrations were carried out with use of the Beckman pH meter. Curves were plotted of pH against the

volume of acid added, and, from each curve, the amount of acid corresponding to the maximum value of  $d(\text{pH})/dv$  was found.

Fig. 1 shows the titration curves of a typical solution of calcium oxide extracted with glycerol. Curve A is for a solution of calcium oxide in which the ratio of ethanol to glycerol is 4 to 1.

The solution was stirred throughout the titration. The pH values were recorded about 5 minutes after the addition of the acid, and this time interval was adhered to in all the titrations. If, however, the solution is shaken for a longer time, the flat portion of the curve is extended towards the pH-axis.

The curve plotted when this procedure was used showed pronounced kinks, as did those obtained by Assarsson and Bokström.<sup>19</sup> It was also noted that electrodes that had been in use with non-aqueous media responded sluggishly, but not erroneously, when used with aqueous media and *vice versa*. For the sake of uniformity of results, the same set of electrodes was used throughout the investigation for non-aqueous titrations.

*Volumetric determination of calcium oxide*—From the titration curves shown in Fig. 1, it is clear that an indicator that changes colour between pH 4 and 4.5 in the described ethanolic medium could be used for determining the end-point. The choice of indicator, however, remains a matter of trial.

The colour changes of methyl red and phenolphthalein have been shown to be not too satisfactory in ethanolic media. Bromocresol green has been said to give satisfactory colour changes when titrations of calcium oxide extracted with ethylene glycol are carried out in an ethanolic medium.<sup>16</sup> In this instance, in addition to these indicators, alizarin S was tried and was found to be suitable. This indicator gave a perceptible colour change from pink through colourless to pale yellow. The mixed alizarin S - bromocresol green indicator gives a colour change from pink to pale yellow and would seem to be preferable. These colour changes are coincident with the neutralisation point as deduced from the data from the electrometric titrations.

For volumetric determinations, an aliquot (generally 25 ml) of the prepared solution was taken and 3 drops of alizarin S solution were added. Ethanolic hydrochloric acid was added to the solution until the colour changed from pink to colourless by way of a rather faint pink. The titration was continued until the appearance of a yellow colour. The end-point was taken as being just 1 drop before this point, *i.e.*, the point at which the solution was just colourless without any tinge of pink. When the mixed indicator, made by mixing 3 drops of alizarin S solution with 2 drops of bromocresol green solution, was used, the colour passed through violet, pink and faint pink to clear yellow, the end-point being taken as the point at which the colour changed from pink to clear yellow.

The results obtained when this procedure was used are given in Table I.

TABLE I

## EXTRACTION OF CALCIUM OXIDE FROM FRESHLY IGNITED LIME WITH GLYCEROL

Weight of calcium oxide taken for extraction, g	Final volume of solution, ml	Calcium oxide found by—				
		potentiometric titration, %	titration with alizarin S as indicator, %	titration with bromocresol green as indicator, %	titration with mixed alizarin S - bromocresol green as indicator, %	complexometric titration, %
0.1202	250	98.7	98.6	96.8*	—	97.9
0.0782	250	—	99.1	97.3*	—	98.8
0.0956	500	97.1	97.1	—	96.6	—
0.1258	500	98.1	98.5	—	—	98.6
0.3213	500†	—	—	—	98.9	100.00

\* Colour change was graded.

† Industrial methylated spirit was used for the dilution.

With regard to the use of other indicators, it may be noted that, in a particular determination, the recovery of calcium oxide with phenolphthalein as the indicator was as low as about 60 per cent., and in a determination with methyl red as the indicator, the recovery was about 80 per cent.; even the colour change was not sharp. Other indicators, such as bromothymol blue, thymol blue, bromocresol purple, Congo red and rosolic acid were tried, but were found to be unsuitable, as no clear end-point was obtained. When bromocresol

green was used as the indicator, the change of colour was graded and extended over 0.2 ml of 0.05 *N* hydrochloric acid.

*Complexometric titration*—A 10-ml aliquot of the prepared solution was titrated against a standard solution of disodium ethylenediaminetetra-acetate in the usual manner in presence of an ammonium chloride - ammonium hydroxide buffer and with Eriochrome black T as the indicator. Titrations were also carried out after limited dilutions of the extract with double-distilled water free from calcium ions. The complexometric titrations do not present any difficulty, and the results are in fair agreement with those obtained potentiometrically or alkalimetrically (see Table I).

*Effect of addition of ethanol or water on the shift of the end-points*—Aliquots of the prepared solution were diluted to 100 ml with ethanol. In another titration, the aliquot was diluted with water. Potentiometric titration curves for these solutions were obtained by titrating with ethanolic hydrochloric acid.

A potentiometric titration curve for one such solution containing ethanol and glycerol in the ratio of 50 to 1, and another for a solution containing 85 per cent. of water are shown in Fig. 1 (curves B and C, respectively).

It can be seen that there is a difference between curve B and curve A, but the end-point falls at the same titre. However, when a large amount of water is present (see Fig. 1, curve C), the end-point is rather uncertain.

Titrations were also carried out with alizarin S, bromocresol green, and mixed alizarin S - bromocresol green as the indicator. Table II shows some typical results of the titration of the calcium oxide solution on progressive dilution with water.

TABLE II  
EFFECT OF VARIOUS AMOUNTS OF WATER

Weight of calcium oxide taken for titration, g	Amount of water present at the end-point, %	Method of determination	Volume of ethanolic hydrochloric acid required, ml	
0.00629	Nil	Volumetric with alizarin S as indicator	5.47	
	5		5.48	
	10		5.48	
	15		5.47	
	20		5.45	
	25		5.40	
0.00478	30	Potentiometric	5.38	
	Nil		4.10	
	10		4.10	
	90		3.80	
	Nil		Volumetric with mixed alizarin S - bromocresol green as indicator	4.07
				4.06
4.02				
0.00456	Nil	Potentiometric	4.00	
	25		4.00	
	50		4.00	
	70		3.90	
	5		Volumetric with alizarin S as indicator	4.00
				20
50		3.80		
70		3.60		

*Use of an ethanol - water mixture for the final dilution of the extracts*—Ethanol mixed with different amounts of water was used for the final dilutions of glycerol extracts, and it was found that no turbidity developed when a mixture containing up to 10 per cent. of water by volume was used.

The most uniform results are obtained if the lime is soaked overnight in glycerol, digested for 6 to 9 hours and then diluted with at least 90 per cent. ethanol. The determinations can be carried out by titration potentiometrically with ethanolic hydrochloric acid, or volumetrically with alizarin S as the indicator. The colour of the indicator changes from pink to colourless and immediately afterwards to pale yellow. The end-point is taken as the colourless point just before the appearance of the pale yellow. The results are somewhat lower when bromocresol green is used as the indicator. The colour change of bromocresol green is not sharp,



but extends over a definite range. Complexometric titration can be carried out without difficulty and with the same degree of precision as the alkalimetric titration.

#### EXPERIMENTS WITH ETHYLENE GLYCOL AS THE EXTRACTING AGENT—

*Preparation of solution of calcium oxide in ethylene glycol*—A known weight of freshly ignited lime was placed in a conical flask with about 10 ml of anhydrous ethylene glycol. A 40-ml portion of anhydrous ethylene glycol was added and the mixture was allowed to digest on a water bath for 30 to 60 minutes. For complete dissolution, this last step is essential. When cool, the solution was diluted to the required volume with anhydrous ethanol.

*Potentiometric and volumetric titration of the extract*—Aliquots of this solution were titrated potentiometrically against ethanolic hydrochloric acid by using the Beckman pH meter and titration curves were plotted. In this instance also, kinks were observed in the titration curve (see Fig. 2, curve A). From the shape of the titration curve it was expected that an indicator that changes colour at about pH 4.5 in ethanolic media would be suitable. Bromocresol green and alizarin S were tried, and both showed colour changes coincident with the point of maximum  $d(\text{pH})/dv$ .

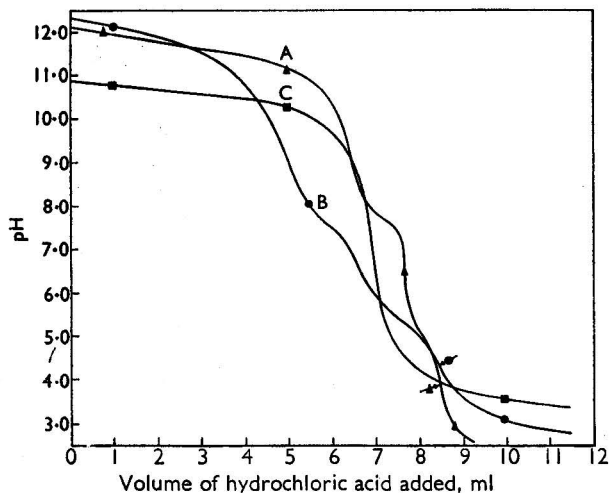


Fig. 2. Titration of calcium oxide extracted with ethylene glycol: curve A, extract with ratio of ethanol to ethylene glycol of 2 to 1; curve B, extract with ratio of ethanol to ethylene glycol of 20 to 1; curve C, extract with ratio of ethanol to ethylene glycol of 2 to 1 containing 90 per cent. of water.

The arrows correspond to the points at which  $\frac{d(\text{pH})}{dv}$  are maxima

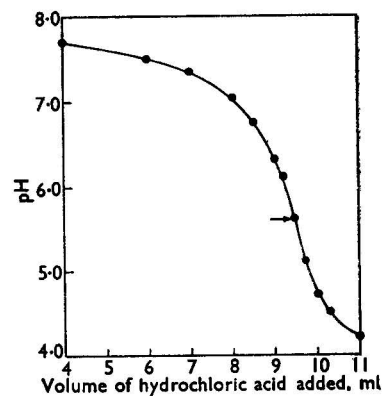


Fig. 3. Titration of calcium oxide extracted with phenol; extract with ratio of ethanol to phenol of 1 to 1 by volume. The arrow corresponds to the point at which  $\frac{d(\text{pH})}{dv}$  is a maximum

*Complexometric titrations*—Complexometric titrations could be carried out without any difficulty. Solutions of freshly ignited lime were prepared in the same manner as before and aliquots were titrated separately against a solution of disodium ethylenediaminetetraacetate and ethanolic hydrochloric acid. The results of alkalimetric and complexometric determinations are shown in Table III.

*Effect of dilution with ethanol, water and ethanol - water mixtures*—Aliquots of the prepared solution were diluted with large volumes of ethanol and water, and titration curves were plotted. These curves are shown, in Fig. 2 (curves B and C, respectively). It can be seen that, although the position of the plot is different on curve B, the maximum value of  $d(\text{pH})/dv$ , occurs at the same point as on curve A. Also, although the end-point can be correctly determined by potentiometric titration, it becomes less distinct if alizarin S or bromocresol green is used as the indicator when the ratio of ethanol to ethylene glycol in the titration medium exceeds 4 to 1. The end-point can be best judged when the ratio of ethanol to ethylene glycol is between 2 to 1 and 4 to 1.

TABLE III

EXTRACTION OF CALCIUM OXIDE FROM FRESHLY IGNITED LIME WITH ETHYLENE GLYCOL

Weight of calcium oxide taken for extraction, g	Final volume of solution, ml	Calcium oxide found by—				
		potentiometric titration, %	titration with alizarin S as indicator, %	titration with bromocresol green as indicator, %	titration with mixed alizarin S - bromocresol green as indicator, %	complexometric titration, %
0.2516	500	99.2	99.2	98.3	—	—
0.2546	500	95.1	95.1	94.5	—	—
0.1382	250	—	100.0	99.5	—	98.9
0.2820	500*	—	—	—	100.0	100.4

\* Industrial methylated spirit was used for the dilution.

When the solution is diluted with a large amount of water, the shape of the curve is entirely different and the end-point is uncertain (see Fig. 2, curve C). In another experiment, an aliquot of the prepared solution was diluted with ethanol containing different proportions of water so that the ratio of ethanol to ethylene glycol did not exceed 4 to 1, and the end-point was determined with alizarin S as the indicator. The results of these experiments are shown in Table IV.

TABLE IV

EFFECT OF VARIOUS AMOUNTS OF WATER

Weight of calcium oxide taken for titration, g	Amount of water present at the end-point, %	Method of determination	Volume of ethanolic hydrochloric acid required, ml
0.0125	Nil	Potentiometric	11.0
	Nil	Volumetric with alizarin S as indicator	11.0
	12		11.0
	20		10.93
	30	Volumetric with bromocresol green as indicator	10.90
	Nil		10.90
12	10.85		

It can be seen from the results that visual titrations can be satisfactorily carried out when the water content of the titration medium does not exceed 10 per cent. The results when ethanol of greater dilution is used are not accurate.

The following conclusions can be drawn—

- (i) Calcium oxide can be extracted readily if ethylene glycol is used as the extracting agent.
- (ii) The extract can be diluted with commercial rectified spirit or industrial methylated spirit, the permissible ratio of rectified spirit to ethylene glycol being between 2 to 1 and 4 to 1, and this solution can be titrated with ethanolic hydrochloric acid potentiometrically, or visually with bromocresol green or alizarin S as the indicator.
- (iii) The determination of calcium oxide in these solutions can be carried out complexometrically without any difficulty.
- (iv) If the solution is diluted excessively with ethanol, the end-point of the titration can be found potentiometrically, but not volumetrically. This difficulty can be obviated by diluting with a mixture of ethanol and ethylene glycol so that the ratio of 4 to 1 is not exceeded.
- (v) If the solution is diluted excessively with water, calcium oxide tends to be precipitated, and no proper titrations can be carried out potentiometrically or visually.
- (vi) Only a limited amount of water can be tolerated in the ethanol used for preparing the solution; 90 per cent. ethanol appears to be suitable.

## EXPERIMENTS WITH PHENOL AS THE EXTRACTING AGENT—

*Preparation of solution of calcium oxide in phenol*—A known weight of freshly ignited lime was transferred to a conical flask containing about 10 ml of a 1 + 1 mixture of phenol and

ethanol. A further 40-ml portion of this mixture was added and the whole was digested on a water bath for 30 to 60 minutes. When cool, the solution was diluted with ethanol to a known volume.

*Potentiometric and volumetric titrations*—An aliquot of the prepared solution was titrated with ethanolic hydrochloric acid and the titration curve was plotted. A very smooth and regular curve was obtained (see Fig. 3) with a maximum value of  $d(\text{pH})/dv$  at pH 5.5 to 5.6. This point corresponds to the pH at which methyl red changes colour. Methyl orange has been used as the indicator for titrations of phenol-extracted calcium oxide, but the results were rather high; in one test the recovery was about 116 per cent. The colour change was not sharp and was, on the whole, unsatisfactory. Table V gives typical results of the titration of phenol-extracted calcium oxide with ethanolic hydrochloric acid.

TABLE V

## EXTRACTION OF CALCIUM OXIDE FROM FRESHLY IGNITED LIME WITH PHENOL

The final volume of each solution was 250 ml

Weight of calcium oxide taken for extraction, g	Calcium oxide found by—		
	potentiometric titration, %	titration with mixed methyl red - methylene blue as indicator, %	
		titration with mixed methyl red - methylene blue as indicator, %	complexometric titration, %
0.0588	98.0	98.0	99.4
0.0922	100.5	100.5	100.8
0.1190	98.5	98.8	99.1
0.1214	—	98.9	98.1

From the titration data it is clear that accurate values of calcium oxide content can be found by using a mixed methyl red - methylene blue indicator. The end-point with this indicator is coincident with the end-point found by potentiometric titration.

*Complexometric titration*—Complexometric titrations were carried out in the manner previously described, and the results have been included in Table V.

It was observed that the complexometric and alkalimetric titrations could be easily carried out and did not present any unusual difficulty. It was also noticed that, in the phenolic solution, a much larger amount of water could be tolerated than in the glycerol and ethylene glycol solutions.

## COMPARATIVE TESTS ON THE SPEED AND PRECISION OF DIFFERENT METHODS OF EXTRACTING CALCIUM OXIDE—

Comparative tests were made on the speed and performance of the different extracting solutions and the titration procedures, all the tests from the initial extractions to the final titrations being carried out on the same batch of freshly ignited lime. The results are shown in Table VI.

TABLE VI

## COMPARISON OF RESULTS WITH DIFFERENT EXTRACTING SOLVENTS

The final volume of each solution was 250 ml

Ex-tracting solvent	Weight of calcium oxide taken for extraction, g	Time of digestion, hours	Ratio of ethanol to ex-tracting solvent	Calcium oxide found by—				
				potentio-metric titration, %	titration with mixed methyl red - methylene blue as indicator, %		complexo-metric titration, %	
					titration with alizarin S as indicator, %	titration with bromo-cresol green as indicator, %		titration with mixed methyl red - methylene blue as indicator, %
Glycerol ..	0.1202	6 to 8	5 to 2	98.7	98.56	96.79	—	97.92
Ethylene glycol ..	0.1382	1 to 2	4 to 1	—	100.02	99.50	—	98.74
Phenol ..	0.1160	½ to 1	4 to 1	—	—	—	98.34	97.82

## CONCLUSIONS

We have used ethanolic hydrochloric acid for the alkalimetric titrations. From the preliminary experiments, it was noted that the course of titration of the extracted calcium oxide with an acid in an ethanolic medium was entirely different from that in an aqueous medium. Since not more than a limited amount of water could be tolerated in the ethylene glycol - ethanol or glycerol - ethanol titration media containing the extracted calcium oxide, an ethanolic solution of acid was used in preference to an aqueous solution. This eliminated the possibility of exceeding the 10 per cent. limit of water in these media, above which the end-point could not be satisfactorily detected. The choice of the acid depended upon the fact that, whereas hydrochloric acid gave a clean potentiometric titration, sulphuric acid caused precipitation of calcium sulphate, which impaired the potentiometric titration. It was further noted that the concentration of the ethanolic hydrochloric acid remained fairly constant. In view of these considerations, ethanolic hydrochloric acid has been used in the proposed procedure.

Another point that can be emphasised is that the solvents used for extraction, *viz.*, glycerol, ethylene glycol, phenol and ethanol, should be as free from water as possible. If filtration becomes necessary, as when silicate products are being tested, washing should also be carried out with dry ethanol. Ethanol containing not more than 10 per cent. of water, or industrial methylated spirit, can, however, be used for the final dilution of the solutions without any effect on the results.

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# The Ebullioscopic Micro-determination of Molecular Weight: An Improved Micro Form of the Menzies - Wright Ebulliometer

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The construction and operation of an improved apparatus for the micro-determination of molecular weight by the Menzies - Wright method is described, and some of the results of the determinations of molecular weights ranging from about 200 to 1000, with benzene, carbon tetrachloride and ethanol as solvents, are given. The volume of solvent used is about 3 ml and the weight of sample varies from about 3 to 15 mg, according to the molecular weight of the substance.

Expressed as coefficients of variation, the accuracy and precision of the method for molecular weights in the region of 200 are 1.8 and 1.3 per cent., respectively, with benzene as the solvent. The corresponding values with carbon tetrachloride as the solvent are 2.3 and 2.1 per cent.

The ebulliometer is unsuitable for use with solvents of higher boiling-point, *e.g.*, dioxan and toluene, because they give unstable readings on the differential thermometer.

In an earlier publication,<sup>1</sup> a modified Menzies - Wright<sup>2</sup> ebulliometer incorporating an internal electric heater and a water-filled differential thermometer was described. This apparatus is suitable for the determination of molecular weights up to about 1000, by using 6 ml of solvent and about 50 mg of sample. If about 20 mg of a suitable substance, *e.g.*, anthracene, are first added to the solvent in the ebulliometer, the sample weight can be reduced to about 10 mg for the determination of molecular weights in the region of 200, but recovery of the sample for other work is then difficult. So that various determinations, in addition to molecular weight, could be carried out when the amount of sample available was small, *e.g.*, 20 to 30 mg, we required an ebulliometer capable of giving results accurate to about 2 per cent. on about 10 mg of sample, which could be recovered by simple evaporation of the solvent. A smaller version of the ebulliometer just described was constructed for use with about 3 ml of solvent, but this apparatus failed to give stable thermometer readings. The results were similar with an ebulliometer designed for use with an external electric heater. This apparatus was similar to the ebulliometer described by Smith and Milner,<sup>3</sup> in which smooth boiling of the solvent is promoted by a tungsten wire sealed through the base of the boiler. In place of the small gas flame used by Smith and Milner, a tubular electric heater, which formed a close fit on the protruding tungsten wire, was used to boil the solvent. This heater was later replaced by one designed to heat the tungsten wire and also a portion of the base of the boiler, but with neither apparatus was satisfactory stability of the thermometer readings obtained. Finally, experiments were carried out with an ebulliometer heated by the carefully controlled flame of a microburner, and the results were satisfactory when benzene, carbon tetrachloride or ethanol was used as the solvent. The failure of all attempts to use solvents of higher boiling-point, such as toluene or dioxan, suggests that ebullimeters having a small capacity, of the type described in this paper and in an earlier publication,<sup>1</sup> cannot be operated with solvents that boil above about 80° C.

## EXPERIMENTAL

### APPARATUS—

The assembled apparatus is shown in Fig. 1 and the various components are shown in Figs. 2 to 6. The ebulliometer, supported on a Perspex pillar (see Fig. 1), is enclosed in a case of the same material 22 inches high, 13 inches wide and 10 inches from back to front. The top of the case is open and the front is fitted with a sliding panel that gives access to the lower part of the apparatus. A constant-level device, not shown in the diagrams, is connected between the tap-water supply and the condenser. A one-mark pipette suitable for the accurate delivery of a fixed volume of solvent is shown in Fig. 8. The mouth of the

pipette should be closed by a small drying tube to prevent the entry of moisture. A suitable device for the transference of viscous or mobile liquid samples to the ebulliometer is shown in Fig. 7. Solid samples are usually introduced in the form of pellets prepared in an Orthofer<sup>4</sup> tablet press.

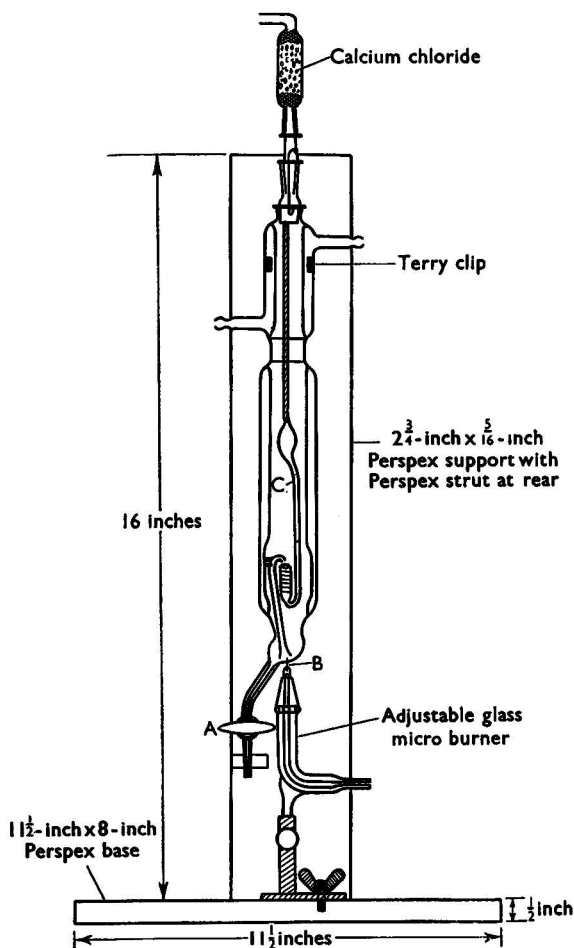


Fig. 1

Fig. 1. Assembled micro-ebulliometer

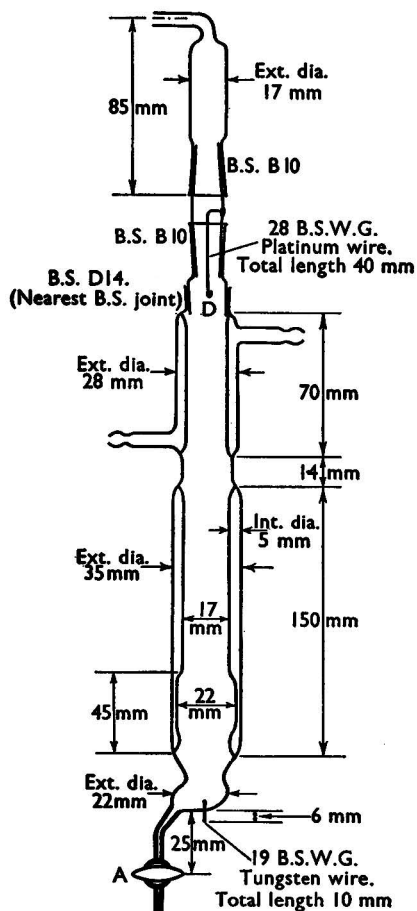


Fig. 2

Fig. 2. Detail of micro-ebulliometer

#### PRELIMINARY EXPERIMENTS—

Much of the preliminary work undertaken to determine the best operating conditions for the gas-heated ebulliometer was concerned with the effect of variation of the volume of solvent, the height of the gas flame and the relative positions of the Cottrell pump and the differential thermometer. In the course of this work, it was noted that when the ebulliometer was in operation, the temperature inside the Perspex case gradually increased during a period of about 1 hour and then remained nearly constant at about 1° C above the initial temperature.

In order to determine what effect, if any, this temperature change might have on the "zero" reading of the differential thermometer, the following experiment was carried out. The capillary tube above the tap, A (Fig. 1), was filled with mercury and a fixed volume of carbon tetrachloride was transferred to the ebulliometer from the one-mark pipette. Tap-water was then circulated through the condenser at a rate of about 50 ml per minute and the

gas flame under the boiler was adjusted to enclose about one-half of the length of the projecting tungsten wire, B (Fig. 1). Twenty minutes later the position of the meniscus in the longer limb of the thermometer, C (Fig. 1), was observed with a cathetometer, and further readings were taken at intervals of 2 to 10 minutes over a period of about 100 minutes. The results are shown in Fig. 9, in which the measured changes in height of the "zero" reading of the thermometer have been converted into the corresponding temperature differences by applying the appropriate factor from the table given by Menzies.<sup>5</sup> The curve shows that, although prolonged boiling of the solvent tends to raise the "zero" reading of the thermometer by a significant amount, the change during short periods, *e.g.*, 10 minutes, is too small to cause

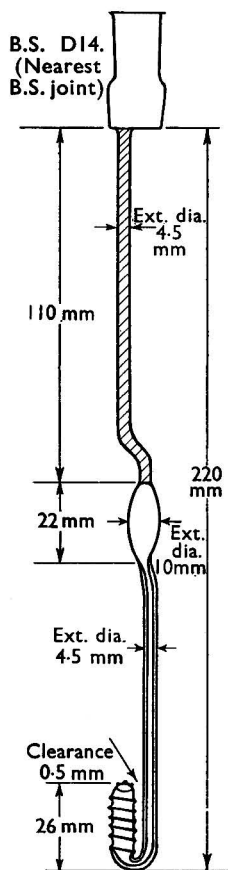


Fig. 4

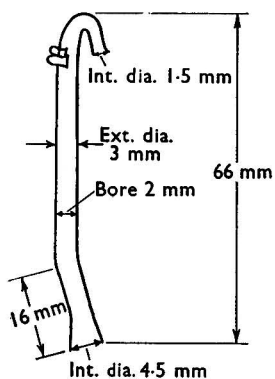


Fig. 3

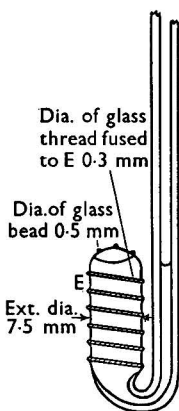


Fig. 5

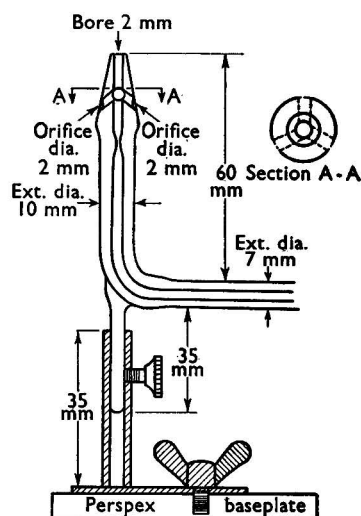


Fig. 6

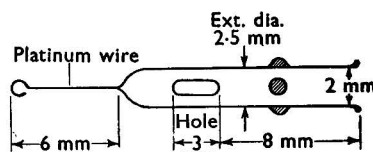


Fig. 7

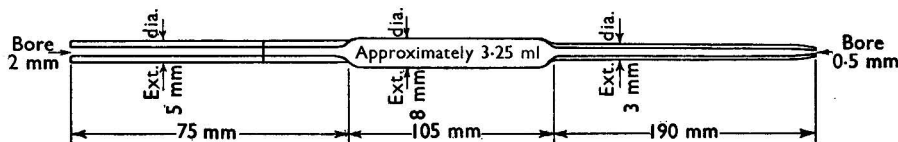


Fig. 8

- Fig. 3. Cottrell pump
- Fig. 4. Differential thermometer
- Fig. 5. Detail of differential thermometer
- Fig. 6. Detail of glass microburner
- Fig. 7. Device for adding liquid samples
- Fig. 8. Pipette for dispensing solvents

serious error in the determination of molecular weight. It is also apparent from the curve that the 10-minute period beginning 20 minutes after lighting the burner is a suitable interval in which to complete a determination, if the sample can be dissolved and the necessary measurements made within this time. This 10-minute period has been adopted in the normal procedure described in this paper, because the complete dissolution of the sample does not usually require more than 5 minutes.

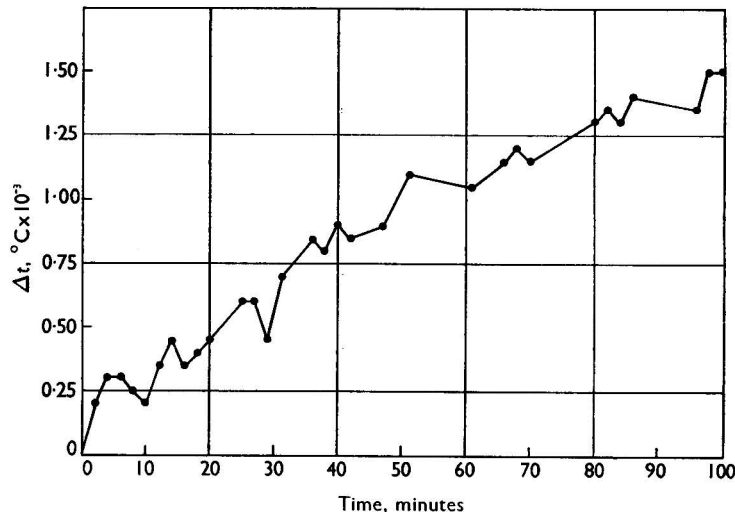


Fig. 9. Variation of temperature difference with time

For substances requiring between about 5 and 30 minutes for complete dissolution, a modified procedure has been developed. In this modified method, the "zero" reading of the thermometer is determined in the usual manner, and the solvent is then allowed to cool to room temperature. The sample is added to the cold solvent, the thermometer reading is recorded 20 minutes after lighting the microburner, and the determination is completed in the usual manner.

The "zero" reading already obtained can be used in further determinations of molecular weight with fresh portions of solvent. It is self-evident that the results by this modified method cannot be accurate unless the "zero" thermometer reading is reproducible to within narrow limits. The results in the following experiments show that this condition is in fact satisfied. A fixed volume of carbon tetrachloride was transferred to the ebulliometer from the one-mark pipette, water was circulated at a rate of about 50 ml per minute through the condenser and the flame of the microburner was adjusted to enclose about one-half of the length of the protruding portion of the tungsten wire. The "zero" reading of the thermometer was recorded after 20 minutes, and further measurements were made at intervals of 2 minutes over a period of 10 minutes. The solvent was allowed to cool to room temperature and then a second set of readings was taken as before. This sequence of operations was repeated until four series of measurements had been made. In the four series, the final "zero" readings showed satisfactory agreement with each other. The observed values, expressed as cathetometer readings, ranged from 779.40 to 779.44 mm. In a further experiment, the reproducibility of the "zero" readings with successive equal volumes of carbon tetrachloride was determined. The measurements were made at intervals of 2 minutes over a period of 10 minutes, as in the first experiment. Before the introduction of any fresh portion of solvent, a stream of warm dry air was passed through the ebulliometer for about 15 minutes. The final "zero" readings in these four series of measurements were again in close agreement with each other, the range of the observed values being from 779.38 to 779.41 mm.

#### METHOD

#### APPARATUS—

The various pieces of apparatus, shown in Figs. 1 to 8, have already been described, p. 169.



## SOLVENTS—

*Benzene*—"Benzene for molecular weight determination," obtainable from the British Drug Houses Limited, dried and stored over sodium wire.

*Carbon tetrachloride*—Pure carbon tetrachloride, obtainable from Hopkin and Williams Limited, used without further treatment.

*Ethanol, absolute*—Purified as follows. To 500 ml of absolute ethanol add a mixture of 3 ml of concentrated sulphuric acid and 10 ml of distilled water. Distil off the ethanol and boil it under reflux with 5 g of silver nitrate and 0.5 g of potassium hydroxide for about 1 hour. Distil as before and boil the distillate under reflux with about 250 g of lump quicklime for several hours. Distil off the ethanol and transfer it, in portions of about 8 ml each, to a series of glass ampoules previously dried in an oven and cooled with a stream of dry nitrogen passing through them. Seal each ampoule and store them in the dark.

NORMAL PROCEDURE FOR DETERMINATION OF THE CONSTANT,  $K$ —

By using the one-mark pipette, transfer a fixed volume of the selected solvent to the ebulliometer. Adjust the rate of flow of water through the condenser to about 50 ml per minute, light the microburner and adjust the flame to enclose half the length of the tungsten wire projecting from the base of the ebulliometer; any convenient type of regulator capable of fine control can be used. After 20 minutes, determine the position of the meniscus in the longer limb of the differential thermometer by using a cathetometer, and repeat the measurement at intervals of 1 minute until two successive readings agree to within about 0.02 mm. Not more than about 5 minutes should be required to complete the determination of the "zero" thermometer reading. Add a weighed pellet (about 8 mg) of pure dry benzil and record the thermometer reading at intervals of 1 minute, as before. Finally, determine the boiling-point of the solvent to the nearest 0.1° C by using a short-stem thermometer suspended in the vapour of the boiling solution. It is not advisable to determine the boiling-point before adding the benzil, because this addition cannot afterwards be made without first withdrawing the thermometer and with it a small amount of the solvent. Calculate the value of the constant,  $K$ , from the formula—

$$K = \frac{210.22 \times (R - Z) \times F}{W},$$

where 210.22 = molecular weight of benzil,

$Z$  = "zero" thermometer reading in mm,

$R$  = thermometer reading after addition of benzil in mm,

$F$  = factor for conversion of  $(R - Z)$  mm to elevation of boiling-point in ° C, and

$W$  = weight of benzil in mg.

To clean the apparatus in readiness for further determinations, drain off the solution through tap A, add about 3 ml of pure benzene to the ebulliometer, boil until the vapour reaches the uncooled condenser and drain off as before. Repeat these operations twice more and then pass warm dry air through the apparatus for about 15 minutes.

## NORMAL PROCEDURE FOR THE MICRO-DETERMINATION OF MOLECULAR WEIGHT—

Determine the "zero" thermometer reading, as already described, and add an accurately weighed amount of the sample to the boiling solvent. Record the new thermometer reading and then determine the boiling-point of the solvent. Calculate the molecular weight of the sample from the formula—

$$M = \frac{K \times W}{(R - Z) \times F}$$

where  $K$ ,  $R$ ,  $Z$  and  $F$  have the same meaning as before, and  $W$  is the weight of sample in mg.

If the sample is a viscous or mobile liquid, weigh it in the small tube shown in Fig. 7; attach the tube to the end of a thin platinum wire, and suspend it from the platinum hook, D (Fig. 2), so that the sample and tube are immersed in the solvent. Withdraw the tube after a few minutes and complete the determination as described.

MODIFIED PROCEDURE FOR DETERMINATION OF THE CONSTANT,  $K$ —

Determine the "zero" reading of the thermometer in the usual way, and then allow the solvent to cool to room temperature. Add an accurately weighed pellet of benzil to the cold

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 solvent, light the microburner under the ebulliometer and complete the determination as  
 in the normal procedure.

MODIFIED PROCEDURE FOR THE MICRO-DETERMINATION OF MOLECULAR WEIGHT—

Determine the "zero" reading of the thermometer, allow the solvent to cool to room  
 temperature and add an accurately weighed amount of the sample. Light the microburner

TABLE I  
 DETERMINATION OF THE CONSTANT,  $K$ , BY THE NORMAL PROCEDURE

Weight of benzil, mg	Boiling-point of solvent, ° C	$F \times 10^3$	$(R-Z)$ , mm	$K$
<i>With benzene as solvent—</i>				
7.955	80.5	4.884	8.10	1.05
7.747	80.5	4.884	8.07	1.04
6.982	80.5	4.884	7.03	1.03
7.200	80.6	4.867	7.20	1.02
6.751	80.4	4.901	6.72	1.03
				Mean value of $K = 1.03$
<i>With carbon tetrachloride as solvent—</i>				
4.407	76.7	5.578	4.90	1.30
5.171	77.0	5.520	5.80	1.30
5.118	77.0	5.520	5.82	1.32
4.632	76.6	5.598	5.26	1.34
4.809	76.6	5.598	5.41	1.32
4.528	76.6	5.598	5.17	1.34
				Mean value of $K = 1.32$
<i>With ethanol as solvent—</i>				
7.698	78.6	5.218	3.37	0.48
9.130	78.6	5.218	4.16	0.50
8.430	78.6	5.218	3.77	0.49
7.864	78.6	5.218	3.44	0.48
				Mean value of $K = 0.49$

TABLE II

ACCURACY AND PRECISION OF THE RESULTS OF THE MICRO-DETERMINATION OF THE MOLECULAR  
 WEIGHT OF ANTHRACENE BY THE NORMAL PROCEDURE WITH BENZENE AS SOLVENT

Weight of anthracene, mg	Molecular weight found	Weight of anthracene, mg	Molecular weight found	Weight of anthracene, mg	Molecular weight found
8.322	179	6.276	174	3.007	175
7.838	175	6.389	177	2.650	179
8.124	171	6.216	175	2.215	172
7.514	178	5.934	176	2.172	177
7.740	176	6.310	177	2.650	178
		6.041	177		
True molecular weight = 178.22		Coefficient of variation from true value = 1.8%			
Mean molecular weight found = 176.0		Coefficient of variation from mean value = 1.3%			

TABLE III

ACCURACY AND PRECISION OF THE RESULTS OF THE MICRO-DETERMINATION OF THE  
 MOLECULAR WEIGHT OF ANTHRACENE BY THE NORMAL PROCEDURE WITH CARBON  
 TETRACHLORIDE AS SOLVENT

Weight of anthracene, mg	Molecular weight found	Weight of anthracene, mg	Molecular weight found	Weight of anthracene, mg	Molecular weight found
9.255	182	6.344	183	3.481	176
5.820	180	6.108	178	8.855	181
6.274	184	3.590	173	8.341	183
		3.228	176		
True molecular weight = 178.22		Coefficient of variation from true value = 2.3%			
Mean molecular weight found = 179.6		Coefficient of variation from mean value = 2.1%			

TABLE IV

 MICRO-DETERMINATION OF MOLECULAR WEIGHT BY THE NORMAL PROCEDURE  
 WITH BENZENE AS SOLVENT

Compound used	Weight taken, mg	Molecular weight found	Molecular weight calculated	Error,* %
Sulphonal .. .. .	7.892	229	228.32	+ 0.5
	7.730	229	228.32	+ 0.5
	7.726	234	228.32	+ 2.5
Cholesterol .. .. .	7.237	396	386.64	+ 2.5
	8.153	399	386.64	+ 3.0
	7.835	402	386.64	+ 4.0
$\beta\beta$ -Bis-(3:5-dibromo-4-methoxy-phenyl)propane .. .. .	9.321	539	571.96	- 6.0
	8.760	559	571.96	- 2.5
	9.724	565	571.96	- 1.0
5:6:7:5':6':7'-Hexa-acetoxy-3:3:3':3'-tetramethylbis-1:1'- <i>spiro</i> hydrindine .. .. .	7.103	607	624.6	- 3.0
	8.360	615	624.6	- 1.5
	8.653	634	624.6	+ 1.5
5:6:7:5':6':7'-Hexabenzoxo-3:3:3':3'-tetramethylbis-1:1'- <i>spiro</i> hydrindine .. .. .	7.922	1052	997	+ 5.5
	7.377	1059	997	+ 6.0
	7.210	1035	997	+ 4.0
	7.366	1035	997	+ 4.0
	14.479	1021	997	+ 2.5
	15.530	1042	997	+ 4.5
	16.222	1031	997	+ 3.5

\* The figures in this column are given to the nearest 0.5 per cent.

TABLE V

 MICRO-DETERMINATION OF MOLECULAR WEIGHT BY THE NORMAL PROCEDURE  
 WITH CARBON TETRACHLORIDE AS SOLVENT

Compound used	Weight taken, mg	Molecular weight found	Molecular weight calculated	Error,* %
Benzophenone .. .. .	7.277	186	182.21	+ 2.0
	7.058	187	182.21	+ 2.1
	7.367	226	222.23	+ 1.5
Ethyl phthalate .. .. .	8.236	233	222.23	+ 5.0
	7.263	226	222.23	+ 1.5
	7.224	224	222.23	+ 1.0
	7.117	227	222.23	+ 2.0
	8.884	229	228.32	+ 0.5
Sulphonal .. .. .	8.342	228	228.32	+ 0.0
	8.726	231	228.32	+ 1.0
	0.707	226	228.32	- 1.0
	0.815	235	228.32	+ 3.0
	1.070	230	228.32	+ 1.0
	0.898	226	228.32	- 1.0
	6.464	250	254.49	- 2.0
Octadecane .. .. .	7.632	262	254.49	+ 3.0
	8.215	251	254.49	- 1.5
	8.600	394	386.64	+ 2.0
Cholesterol .. .. .	8.092	386	386.64	0.0
	8.292	394	386.64	+ 2.0
	9.148	487	506.95	- 4.0
Hexatriacontane .. .. .	9.332	502	506.95	- 1.0
	9.201	516	506.95	+ 2.0
	8.584	557	571.96	- 2.5
$\beta\beta$ -Bis-(3:5-dibromo-4-methoxy-phenyl)propane .. .. .	8.676	558	571.96	- 2.5
	9.679	565	571.96	- 1.0

\* The figures in this column are given to the nearest 0.5 per cent.

and complete the determination as in the normal procedure. After the ebulliometer has been cleaned and dried, further determinations of molecular weight can be carried out with fresh portions of solvent without repeating the determination of the "zero" thermometer reading.

#### RESULTS—

The results by the normal procedure for the determination of the constant,  $K$ , with benzil being used as the solute and with benzene, carbon tetrachloride and ethanol as solvents, are given in Table I. The precision and accuracy of the normal procedure for the determination of molecular weights in the region of 200 is shown by the results given in Tables II and III for anthracene, with benzene and carbon tetrachloride as solvents. Further results for the determination of molecular weights ranging from about 200 to 1000, with benzene, carbon tetrachloride and ethanol as solvents, are given in Tables IV, V and VI.

TABLE VI

MICRO-DETERMINATION OF MOLECULAR WEIGHT BY THE NORMAL PROCEDURE  
WITH ETHANOL AS SOLVENT

Compound used	Weight taken, mg	Molecular weight found	Molecular weight calculated	Error,* %
Phenacetin .. .. .	4.373	180	179.21	+ 0.5
	4.101	171	179.21	- 4.5
	4.216	174	179.21	- 3.0
	4.347	174	179.21	- 3.0
Sulphonal .. .. .	7.695	219	228.32	- 4.0
	7.956	226	228.32	- 1.0
	7.140	234	228.32	+ 2.5
	8.210	222	228.32	- 3.0
$\beta\beta$ -Bis-(3:5-dibromo-4-methoxy-phenyl)propane .. .. .	8.914	538	571.96	- 6.0
	9.822	545	571.96	- 4.5
	9.318	580	571.96	+ 1.5
	8.964	552	571.96	- 3.5
5:6:7:5':6':7'-Hexa-acetoxy-3:3:3':3'-tetramethylbis-1:1'- <i>spiro</i> hydrindine .. .. .	8.125	623	624.60	- 0.5
	8.547	586	624.60	- 6.0
	8.528	598	624.60	- 4.5
	8.262	598	624.60	- 4.5

\* The figures in this column are given to the nearest 0.5 per cent.

The constant,  $K$ , was determined by the modified procedure with carbon tetrachloride, b.p. 76.8° C, as the solvent, and the value of  $F \times 10^3$  was 5.558; the results were as follows—

Weight of benzil, mg .. .. .	4.506	5.308	4.869	4.996
( $R - Z$ ), mm .. .. .	4.91	5.76	5.28	5.48
$K$ .. .. .	1.27	1.27	1.27	1.28

These results give a mean value for  $K$  of 1.27. Some determinations of the molecular weight of cholesterol, molecular weight 386.64, were carried out by the modified procedure with carbon tetrachloride as the solvent; the results were as follows—

Weight of cholesterol taken, mg .. .. .	8.504	8.167	8.068	7.914
Molecular weight found .. .. .	383	392	391	396
Error, % .. .. .	- 1.0	+ 1.5	+ 1.0	+ 2.5

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## Notes

### SPECTROPHOTOMETRIC DETERMINATION OF URANIUM IN ORGANIC-SOLVENT SOLUTIONS

WHEN uranium, either from natural sources or irradiated material, is extracted by a liquid - liquid extraction method, the need arises for an easy and rapid method of determining it in the organic phase. Usually, uranium is extracted from the organic phase by one of the numerous known methods. As small volumes of solution are generally used, the possibility of error is great, since the complete separation of phases is seldom possible in practice. Another method consists in the decomposition of the organic phase with a mixture of sulphuric and perchloric acids before the determination, but this is time-consuming and is seldom convenient.

Very few workers have dealt with the direct determination of uranium in organic solutions. Fisher and Thomason<sup>1</sup> have proposed a polarographic method for the direct determination of uranium. This method is limited to uranium present in a solution of tri-*n*-butyl phosphate diluted with *isopropyl* ether, the concentration of tri-*n*-butyl phosphate being between 5 and 30 per cent. The general application of this method is prevented, since the concentrations of tri-*n*-butyl phosphate used often exceed these limits and also many other substances are used as diluents, the most frequent being different varieties of kerosine.

Among the proposed spectrophotometric methods, the acetone - ammonium thiocyanate method<sup>2</sup> is used for the direct determination of uranium in organic solutions. The possibilities of adapting this method are limited. Nietzel and De Sesa<sup>3</sup> have applied it to solutions of uranium in ethyl acetate, Sinyakova and Novikov<sup>4</sup> to solutions of uranium in ethyl methyl ketone and Kimball and Rein<sup>5</sup> to solutions of uranium in a mixture of tri-*n*-butyl phosphate and carbon tetrachloride. Kimball and Rein have modified the original method by substituting ethanol for acetone, so as to attain a uniform single phase of the organic solution and the aqueous solution of the reagents. This could not be done with tri-*n*-butyl phosphate diluted with kerosine. Nietzel and De Sesa<sup>6</sup> have recently, in a similar manner, substituted butyl Cellosolve for acetone, so as to avoid many of the disadvantages of the acetone - ammonium thiocyanate method. They applied the method to the determination of uranium in *isobutyl* methyl ketone solutions. Francois<sup>7</sup> produced a coloured complex by adding a solution of uranium in tri-*n*-butyl phosphate and *isooctane* to a solution of dibenzoylmethane in acetone and water.

#### EXPERIMENTAL

We have attempted to develop a method that is rapid and sensitive under different conditions. The idea was to combine two of the steps of the analytical procedure that are usually performed separately, *viz.*, the extraction of the uranium from the organic phase with a complexing agent and the development of the colour in the aqueous phase with the same complexing agent to permit the absorptiometric determination. As this was achieved, there was no necessity for finding a reagent that would form an homogeneous phase with many different organic solvents.

We then investigated the different spectrophotometric methods available for the determination of uranium in aqueous solutions and arrived at the conclusion that the ammonium thioglycolate method of Davenport and Thomason<sup>8</sup> could be used directly without loss of any of its advantages. Owing to the very slight solubility of inorganic substances in organic solvents, the interference caused by some cations and anions in aqueous solutions need scarcely be considered.

#### METHOD

##### REAGENTS—

*Ammonium thioglycolate solution*—Prepared by diluting 10 ml of thioglycolic acid with about 50 ml of water and then neutralising the solution with diluted ammonia solution and adjusting the volume to 100 ml by adding more water.

*Ammonia solution, diluted (1 + 1)*—Prepared by diluting analytical-reagent grade ammonia solution, sp.gr. 0.880, with water.

##### PROCEDURE—

An aliquot of the organic solution is transferred to a 25-ml calibrated flask by using a micro-pipette, which is then washed with the pure organic solvent, the washings being added to the flask, and 2 ml of diluted ammonia solution (1 + 1) and 2 ml of ammonium thioglycolate

solution are added. The flask is then shaken well and the aqueous layer is made up to the mark by adding water. On standing for a few minutes, the two phases separate completely, the organic layer is removed either by using a pipette or by decantation. The aqueous layer is examined spectrophotometrically in the usual way.

If the separation of the phases requires a longer time, as when solvents having a specific gravity nearly the same as that of water are used, *e.g.*, tri-*n*-butyl phosphate, the formation of the complex can be achieved in a centrifuge tube by adding the reagents quantitatively so that the final volume of the aqueous phase will be exactly 25 ml. Then, after spinning in a centrifuge, the clear aqueous solution is used for the spectrophotometric determination. A similar procedure can be adopted for solvents heavier than water, *e.g.*, tri-*n*-butyl phosphate diluted with carbon tetrachloride.

Because of the very low acidity of the organic phase, *e.g.*, tri-*n*-butyl phosphate in kerosine,<sup>9</sup> as well as the acidity in general, it is not necessary to neutralise the organic phase before the addition of the reagents.

### RESULTS

The proposed method was applied to solutions of uranium in tri-*n*-butyl phosphate, *isobutyl* methyl ketone, ethyl acetate and diethyl ether. The results are shown in Table I. The organic phases were analysed after re-extraction as well as directly by the proposed method.

TABLE I  
DETERMINATION OF URANIUM IN VARIOUS SOLVENTS

Solvent	Uranium found after re-extraction, mg per ml	Uranium found by proposed method, mg per ml	Difference, %
Tri- <i>n</i> -butyl phosphate .. ..	1.632	1.620	-0.7
<i>iso</i> Butyl methyl ketone .. ..	13.100	13.480	+2.9
Ethyl acetate .. .. .	1.407	1.390	-1.2
Diethyl ether .. .. .	9.100	9.250	+1.6

Since the use of tri-*n*-butyl phosphate was of special interest, it was examined in greater detail and in the presence of different diluents. The diluents used were kerosine, diethyl ether, dibutyl ether, *isopropyl* ether, hexane and carbon tetrachloride. The solutions of uranium were prepared by extracting a solution of uranium nitrate with mixtures of tri-*n*-butyl phosphate and the diluent, each mixture containing 30 per cent. of tri-*n*-butyl phosphate. The solutions were analysed after re-extraction as well as directly by the proposed method; the results are shown in Table II.

TABLE II  
DETERMINATION OF URANIUM IN TRI-*n*-BUTYL PHOSPHATE DILUTED WITH  
VARIOUS SOLVENTS

Diluent for tri- <i>n</i> -butyl phosphate	Uranium found after re-extraction, mg per ml	Uranium found by proposed method, mg per ml	Difference, %
Kerosine .. .. .	2.370	2.400	+1.3
Diethyl ether .. .. .	4.865	4.880	+0.3
Dibutyl ether .. .. .	7.155	6.980	-2.4
<i>iso</i> Propyl ether .. .. .	5.965	5.840	-2.1
Hexane .. .. .	18.950	18.900	-0.3
Carbon tetrachloride .. ..	12.130	11.890	-2.0

All the results given in Tables I and II are an average of two determinations.

In order to determine the influence of impurities that can be present in the solvent phase, we analysed the solvent phases obtained by the extraction of solutions of uranium chloride in presence of hydrochloric acid and other chlorides. Extraction was carried out with 30 per cent. of tri-*n*-butyl phosphate in di-*n*-butyl ether. The solvent phase was analysed after decomposition with sulphuric and perchloric acids as well as directly by the proposed method; the results are shown in Table III.

The differences are within the limits of error for the proposed method, thereby indicating that small amounts of the inorganic salts that can be present in the solvent phase do not affect the accuracy of determination.

TABLE III  
DETERMINATION OF URANIUM IN PRESENCE OF VARIOUS CHLORIDES  
Each solution contained *M* hydrochloric acid

Chloride present	Concentration of chloride, <i>M</i>	Uranium found after decomposition with sulphuric and perchloric acids,* mg per ml	Uranium found by proposed method, mg per ml	Difference, %
—	—	0.95	0.94	-1.0
Sodium ..	saturated	18.00	18.04	+0.2
Potassium ..	saturated	6.65	6.74	+1.3
Ammonium ..	5	10.05	9.98	-0.7
Lithium ..	5	11.50	11.68	+1.6
Calcium ..	2.5	20.30	20.84	+2.7
Magnesium ..	2.5	22.40	22.66	+1.2
Aluminium ..	1.67	23.33	23.44	+0.5

\* We thank Dr. I. Gal, who kindly provided these results.

The concentration range investigated was from 0.384 to 1.460 mg of uranium per 25 ml, and in this range Beer's law is obeyed. The colour of the complex formed was stable for 1 hour. Blank values were determined after shaking a solution of the reagents with the same volume of the solvent as was used for the determinations as well as on a solution of the reagents alone. No difference between the blank values was observed when 0.1 to 1 ml of the solvent was shaken with 25 ml of the reagent solution. This indicates that traces of solvent that go into the aqueous phase do not affect the characteristics of the method.

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#### THE DETERMINATION OF CALCIUM IN MILK AND WHEY

THE use of metastannic acid in the preparation of a phosphate-free serum permits a rapid determination of calcium in milk and whey by the ethylenediaminetetra-acetic acid (EDTA) titration method. The sera are free from colloidal matter and lend themselves admirably to the EDTA procedure.

With an increase in the appreciation of the importance of calcium in milk and other biological material, the need has arisen for more rapid and convenient methods for its determination, particularly when many samples have to be examined. Several alternatives to the standard oxalate method have been advanced. In the turbidimetric method of Marier and Boulet,<sup>1</sup> the solution, containing 40 to 100  $\mu\text{g}$  of calcium, is treated with a phosphate-citrate reagent and then with an alkaline gelatin-oleate solution. The resulting turbidity is determined by measuring the optical density at 420  $m\mu$ . Chloranilic acid has been used as a precipitant for calcium in plant-ash<sup>2</sup> and in soil extracts,<sup>3</sup> and the method has been applied to milk-ash by Breyer and McPhillips.<sup>4</sup> In their method, an excess of reagent is added to a hydrochloric acid extract of milk-ash and the excess is determined by measuring the polarographic diffusion current. Two further developments have been the flame-photometric and EDTA titration methods. In both, however, difficulties have been experienced through the presence of orthophosphates. For the flame-photometric determination of calcium, phosphates have been removed by passing the solution through a cation-exchange resin, from which the cations were subsequently released by elution with acid.<sup>5,6</sup> Several workers have dealt with the problem of phosphate interference in the EDTA titration method, some finding it sufficiently troublesome to necessitate special procedures,

whereas others considered it to be very slight. When the solutions were sufficiently dilute to bring the solubility product below that of calcium phosphate, Kenny and Toverud<sup>7</sup> found no interference. It would seem, therefore, that for each level of calcium there should be a concentration of orthophosphate beyond which interference with the EDTA titration can be expected. However, the work of Collier<sup>8</sup> does not entirely substantiate this hypothesis. There was no clear-cut line of demarcation between phosphate concentrations that adversely affected the titration and those without effect, but rather there was a broad band of gradually increasing interference. In this work, the photometric titration apparatus of Fricker<sup>9</sup> was used. In view of these uncertainties, which exist in very dilute solutions, other methods of avoiding phosphate interference have been sought. The back-titration procedure has been used by Mälkki<sup>10</sup> and Stephens,<sup>11</sup> in which the excess of EDTA added to the solution is titrated with a standard calcium solution. At the end-point, addition of 1 drop of calcium solution causes an immediate change in the murexide indicator. As there is a slow formation of calcium phosphate, it is essential that the end-point should be judged by the immediate change in colour of the murexide indicator. It is pointed out by Mälkki that, when the back-titration procedure is used, it is no longer necessary to use carbonate-free sodium hydroxide to adjust the pH of the solution to about 12. Mason<sup>12</sup> considered that this procedure was not altogether satisfactory for routine analysis. His method consists in passing an acid extract of plant-ash through a column of Zeo-Karb 215, eluting with hydrochloric acid, evaporating the effluent to dryness, dissolving the residue in water and titrating with EDTA in the customary manner. Jenness<sup>13</sup> extracted phosphates from an acid milk-ash extract by passing it through the anion-exchange resin, Duolite A4. The solution, after adjustment of pH, can then be titrated satisfactorily with EDTA. Gehrke, Affsprung and Lee<sup>14</sup> used the chloride form of another anion-exchange resin, Amberlite IR-4B, for the same purpose. Collier<sup>15</sup> extracted phosphates by means of a butanol-chloroform-sodium molybdate mixture.

The elimination of phosphates by means of stannic oxide (or metastannic acid) is a well tried method of qualitative analysis. Although the precise mechanism of the method is not fully understood, there are no doubts about its efficiency. Although a search of the literature failed to discover any quantitative application of this reaction, it seemed reasonable that, under the right conditions, metastannic acid could be used to give a phosphate-free milk serum admirably suitable for the EDTA titration method.

#### EXPERIMENTAL

In a number of trials, milk sera were produced under a variety of conditions and were titrated with EDTA after adjustment of the pH to about 12. After a correction had been made for the volume of the precipitate, the resultant values for calcium content were compared with those given by the standard oxalate procedure. In the latter, 25 ml of milk or whey were evaporated to dryness, ignited and ashed at 700° C. The ash was dissolved in hydrochloric acid, and the solution was neutralised and then rendered slightly acid by adding acetic acid. From this solution, calcium was precipitated as oxalate and determined by titration with potassium permanganate.

It was soon apparent that, unless a fairly high level of acidity was maintained throughout the metastannic acid treatment, there was a danger of incomplete recovery of calcium. In these early trials a suspension of metastannic acid was used. Pure tin was treated with the minimum amount of concentrated nitric acid, and the resulting metastannic acid was washed by decantation with water and finally made into an aqueous suspension containing 18 per cent. of stannic oxide. It was evident that the amount of metastannic acid needed more precise measurement than was possible with the aqueous suspension. It was preferable, therefore, to add measured volumes of potassium metastannate solution to milk containing the requisite amount of nitric acid. In this manner the two critical factors, acidity and amount of metastannic acid present, were brought under more effective control.

By trial and error the procedure described below was finally adopted, and, as shown by the results in Table I, the method agrees satisfactorily with the standard oxalate procedure, over which it has the advantages of rapidity and convenience.

#### METHOD

##### REAGENTS—

*Potassium metastannate solution*—In an 800-ml beaker, just cover 15 g of pure granulated tin with distilled water and add concentrated nitric acid in small amounts until no more metallic tin remains (about 65 ml). Wash the metastannic acid by decantation, using about 1700 ml of distilled water; pass the wash liquor through an 18-cm Whatman No. 2 filter-paper. Wash the



residue back into the beaker and dissolve the whole by the addition of 5 ml of potassium hydroxide solution (0.71 g of potassium hydroxide per ml) and make the solution up to 250 ml by adding water. The alkalinity of this solution, determined by titration against 0.1 N hydrochloric acid with phenolphthalein as indicator, was 11.6 ml per 10 ml of metastannate solution.

TABLE I  
DETERMINATION OF CALCIUM OXIDE IN MILK AND WHEY

Sample	Calcium oxide found by proposed method, %	Calcium oxide found by oxalate method, %	Difference, %
Individual milk ..	0.151	0.151	0.0
Mid lactation milk ..	0.156	0.157	+0.001
Late lactation milk ..	0.195	0.198	+0.003
Individual milk ..	0.194	0.188	-0.006
	0.164	0.159	-0.005
	0.161	0.163	+0.002
	0.176	0.176	0.0
	0.171	0.170	-0.001
	0.171, 0.171	—	—
	0.230	0.226	-0.004
	0.156	0.155	-0.001
	0.143	0.142	-0.001
	0.163	0.164	-0.001
Individual milk ..	0.185, 0.185	0.185	0.0, 0.0
	0.224	0.223	-0.001
Bulk raw milk ..	0.151	0.150	-0.001
	0.152	0.150	-0.002
Separated milk ..	0.166	0.167	+0.001
Bulk milk ..	0.158, 0.158	0.160	+0.002, +0.002
	0.155	0.158	+0.003
	0.156	0.159	+0.003
Individual milk ..	0.179	0.180	+0.001
	0.130	0.131	+0.001
	0.114	0.119	+0.005
	0.165, 0.166	0.166	+0.001, 0.0
Whey .. ..	0.066	0.067	+0.001
	0.099	0.102	+0.003
	0.070	0.068	-0.002
	0.067	0.064	-0.003
	0.049	0.050	+0.001
	0.073	0.072	-0.001
	0.080	0.079	-0.001
	0.097	0.096	-0.001
	0.137	0.136	-0.001

*Potassium hydroxide solution*—Dissolve 56 g of analytical-reagent grade potassium hydroxide pellets in 44 g of distilled water. By titration against 0.1 N hydrochloric acid this solution was found to contain 0.71 g of potassium hydroxide per ml.

*Nitric acid, diluted (1 + 2)*—Dilute 1 volume of concentrated analytical-reagent grade nitric acid with 2 volumes of distilled water.

*Sodium hydroxide solution, 0.5 N*—Prepare by diluting a 50 per cent. w/w carbonate-free sodium hydroxide solution. Standardise with potassium hydrogen phthalate.

*EDTA solution*—Dissolve 4 g of disodium dihydrogen ethylenediaminetetra-acetate in water and make up to 1 litre.

*Murexide indicator*—Grind 0.1 g of murexide in a mortar with 20 g of analytical-reagent grade potassium sulphate. Store the mixture in a stoppered tube and keep it in a dark cupboard when not in use.

*Standard colour solution*—Add 0.15 ml of cresol red indicator solution (0.1 g of cresol red dissolved in 20 ml ethanol and made up to 100 ml with distilled water) to 60 ml of saturated sodium tetraborate solution.

*Standard calcium solution*—Dry analytical-reagent grade calcium carbonate at 100° C. Weigh accurately about 2 g into a beaker and dissolve it in a minimum amount of dilute hydrochloric acid. Dilute this solution with water and boil to expel carbon dioxide; cool and make up to 1 litre with water.

## PROCEDURE—

Measure 5 ml of milk or whey into a 100-ml calibrated flask. Add about 30 ml of distilled water and then 1 ml of diluted nitric acid (1 + 2). Mix gently, and, with a pipette, add 10 ml of potassium metastannate solution with constant rotation of the flask. Dilute to the mark with distilled water and shake briskly. After a few minutes, pass the solution through an 11-cm Whatman No. 40 filter-paper, rejecting the first few millilitres of filtrate. The filtrate should be perfectly clear, but a slight turbidity has no adverse effect on the titration. With a pipette transfer 50 ml of filtrate to a 150-ml flask, add a small fragment of pH test-paper and neutralise with 0.5 N sodium hydroxide solution. Add a further 2 ml of the sodium hydroxide solution, and, by means of a small glass tube or a suitably marked narrow spatula, add 0.02 to 0.03 g of murexide indicator. Using a 10-ml burette graduated in 0.02 ml, titrate with EDTA solution until the addition of 1 drop changes the colour from pink to the violet shade of the standard. Standardise the EDTA solution by measuring 10 ml of standard calcium solution into a flask containing about 20 ml of distilled water, neutralise with 0.5 N sodium hydroxide solution, add a further 2 ml and titrate with EDTA exactly as described. A blank determination is essential and is carried out exactly as indicated, but with distilled water instead of the sample.

The correction for the volume of precipitate can be determined by comparing the titre for milk with the titre for an identical sample to which a measured volume of standard calcium solution has been added. A typical example is as follows—

*For milk sample—*

50 ml of filtrate required 7.38 ml of EDTA solution.

*For 5 ml of milk plus 5 ml of standard calcium solution—*

50 ml of filtrate required 12.26 ml of EDTA solution.

Difference equivalent to 2.5 ml of standard calcium solution = 4.88 ml.

5 ml of standard calcium solution titrated directly required 9.51 ml of EDTA solution.

$$\text{Correction for volume of precipitate} = \frac{9.51}{2 \times 4.88} \times 100 = 97.4 \text{ per cent.}$$

For the samples examined the correction factor varied from 97.3 to 97.7 per cent.

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## Ministry of Agriculture, Fisheries and Food

### FOOD STANDARDS COMMITTEE

#### REPORT ON THE ICE CREAM STANDARD

THE Minister of Agriculture, Fisheries and Food, the Minister of Health and the Secretary of State for Scotland have approved for publication a Report of the Food Standards Committee on the standard of composition for ice cream.

The report examines the need for revising the Food Standards (Ice Cream) Order, 1953, in the light of present-day conditions and current commercial practice.

Copies of the report may be obtained from H.M. Stationery Office, or from any bookseller, price 8d. (plus postage).

REPORT ON FLUORINE: REVISED RECOMMENDATIONS FOR LIMITS FOR  
FLUORINE CONTENT OF FOODS

THE Minister of Agriculture, Fisheries and Food, the Minister of Health and the Secretary of State for Scotland have approved for publication a Revised Report of the Food Standards Committee's Metallic Contamination Sub-Committee on the fluorine content of foods.

An earlier report was published in June, 1953.

Copies of the Revised Report may be obtained from H.M. Stationery Office, or from any bookseller, price 6d. (plus postage).

**British Standards Institution**

## NEW SPECIFICATIONS\*

- B.S. 573:1957. Di-*n*-butyl Phthalate. Price 4s.
- B.S. 575:1957. Carbon Tetrachloride. Price 4s.
- B.S. 579:1957. Diethyl Ether (Technical). Price 4s.
- B.S. 1999:1957. Tritolyl Phosphate. Price 4s.
- B.S. 2941:1957. Paraformaldehyde. Price 4s.
- B.S. 2942:1957. Formaldehyde Solution. Price 4s.
- B.S. 2943-4:1957. *o*-Dichlorobenzene (Grades A and B). Price 4s. 6d.

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

**Book Reviews**

COMPLEXOMETRIC TITRATIONS. By GEROLD SCHWARZENBACH. Translated and revised in collaboration with the author by HARRY IRVING, M.A., D.Phil., D.Sc., F.R.I.C. Pp. xviii + 132. London: Methuen & Co. Ltd. 1957. Price 21s.

It is important to realise that this book is not just a translation of Schwarzenbach's original work (reviewed in *Analyst*, 1957, **82**, 294), which was first published in 1955. The opportunity has been taken to bring the subject matter up to date, at any rate up to August, 1956, and to embody in it many corrections and additions to the original text. Literature references now number 305, as compared with 181 in the original work. A certain amount of new material has been included, and many new diagrams have been provided. The text has been re-grouped into seven chapters dealing, respectively, with Polyamines and Complexones, Basic Theory of Complexometric Titrations, Indicators Used in Complexometry, Titration of Mixtures, Solutions used in Complexometric Titrations, Details of Procedures and Concluding Remarks.

In reading the book, one has the feeling that, on occasion, the translation has been too literal, e.g., one meets rather unfamiliar phrases such as ". . . the clear liquid standing over the precipitated magnesium hydroxide . . ." p. 71. Then again, though tremendous efforts have been made to effect adequate cross-referencing, this object has not always been achieved, for example, the reader will find adequate cross-references to a type IV reaction in one part of the book, but not in others. The reference to the precipitation of calcium as sulphite on p. 62 should include reference 83 as well as 304. On p. 50, barium has been omitted from the list of metal cations that can be determined complexometrically by direct titration with EDTA. Some of the diagrams could have been improved by much bolder lettering. All these are minor criticisms.

Really Dr. Irving has presented us with an up to date translation of Schwarzenbach's work, which has had such a profound effect on analytical chemistry during the last few years. In doing so, he will, without doubt, enable greater numbers of analytical chemists to take advantage of the many procedures that the introduction of EDTA has provided for the up to date analyst.

This book will have a further function; it will help English readers to establish more firmly the stoichiometry of some of the reactions involved, just as in the 1930's it was necessary to digest a great deal of information about 8-hydroxyquinoline and to place this substance in its correct place as an analytical reagent.

J. HASLAM

FUSION METHODS IN CHEMICAL MICROSCOPY. By WALTER C. McCrone, JUN. Pp. viii + 307. New York and London: Interscience Publishers Inc. 1957. Price \$6.75; 52s.

In 1891, Otto Lehmann observed that the microscopical appearance exhibited on crystallisation of an organic compound from its own melt is usually characteristic. The results of his researches were published in a book entitled "*Die Krystallanalyse*," and he listed a number of

properties that could be determined on crystals from the melt and discussed the value of this technique in studying the phase diagrams of systems of one and two components. Lehmann's work received little attention until, nearly 50 years later, the three Koflers—Ludwig, Adelheid and Walter—along with Marie Brandstätter in Austria and Walter C. McCrone, jun. and his fellow workers in the United States expanded the method. This book describes the technique and gives analytical data for the identification of many organic compounds.

Besides a polarising microscope, the essential accessory is a hot stage, including means for controlling and measuring temperatures over a wide range. Various designs are now available commercially and are described and illustrated in the earlier pages of this book. Then comes a discussion of the various optical properties to be observed during heating, after the compound has melted, during cooling and crystallisation, after cooling is complete and, finally, during re-heating. The refractive index of the melt is the most useful character, and this is determined by the use of a standard set of 24 glass powders covering a range from 1-300 to 1-6877. The last hundred pages of this book comprises four analytical tables giving the data for the identification of 1189 organic compounds. Table I lists the compounds alphabetically with their melting-points and with an identifying code number. Table II lists the compounds by code number in the order of increasing melting-point. Table III gives the eutectic melting-points of each compound with several standard compounds. Table IV gives the temperature at which the melt of the compounds has the same refractive index as a chosen glass standard; for a few compounds this temperature coincides with the melting-point, but for most it is a temperature slightly higher than that at which the compound first melts.

It is stated that, by this method, fusible compounds may be rapidly identified on very small samples and that relatively little specialised training is needed to acquire the technique. However this may be, the author is to be congratulated upon a well planned, fully documented and carefully written exposition of an interesting analytical method. The book, which includes a number of remarkably fine coloured plates, has been excellently produced, and it should have a special appeal to those engaged in research work in organic chemistry. N. L. ALLPORT

## Publications Received

- ORGANIC SYNTHESSES. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Volume 37. Editor-in-Chief: JAMES CASON. Pp. viii + 109. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1957. Price \$4.00; 32s.
- ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. First Supplement Volume. Edited by RAYMOND E. KIRK and DONALD F. OTHMER. Pp. xviii + 974. New York: The Interscience Encyclopedia Inc.; London: Interscience Publishers Ltd. 1957. Price \$25.00; 175s.
- THE ANALYTICAL USES OF ETHYLENEDIAMINETETRAACETIC ACID. By FRANK J. WELCHER. Pp. xviii + 366. Princeton, N.J., New York, Toronto and London: D. Van Nostrand Co. Inc. 1958. Price \$8.50; 64s.
- INTRODUCTION TO PROTEIN CHEMISTRY. By SIDNEY W. FOX and JOSEPH F. FOSTER. Pp. viii + 459. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1957. Price \$9.50; 76s.
- ORGANIC ELECTRODE PROCESSES. By MILTON J. ALLEN. Pp. xiv + 174. London: Chapman & Hall Ltd. 1958. Price 32s.
- SOURCE BOOK OF INDUSTRIAL SOLVENTS. Volume II: HALOGENATED HYDROCARBONS. By IBERT MELLAN. Pp. iv + 267. New York: Reinhold Publishing Corporation; London: Chapman & Hall Ltd. 1957. Price \$7.00; 56s.
- Volume I of this Series was published under the title "Handbook of Solvents" (see Publications Received, Analyst, 1957, 82, 536).*
- INDUSTRIAL CHEMICALS. By W. L. FAITH, DONALD B. KEYES and RONALD L. CLARK. Second Edition. Pp. x + 844. New York: John Wiley & Sons Inc.; London: Chapman and Hall Ltd. 1957. Price \$16.00; 128s.
- CRYSTAL STRUCTURES. Supplement III. By RALPH W. G. WYCKOFF. Loose-leaf, 441 sheets. New York and London: Interscience Publishers Ltd. 1958. Price \$20.00; 150s.
- Supplement III consists of punched leaves for insertion into the binders of Volumes I and II; it comprises additions to chapters I to VIII.*
- THE DEVELOPMENT OF TITRIMETRIC ANALYSIS TILL 1806. By E. RANCKE MADSEN. Pp. 239. Copenhagen: G.E.C. Gads Forlag. 1958. Price Dan. kr. 20.00.

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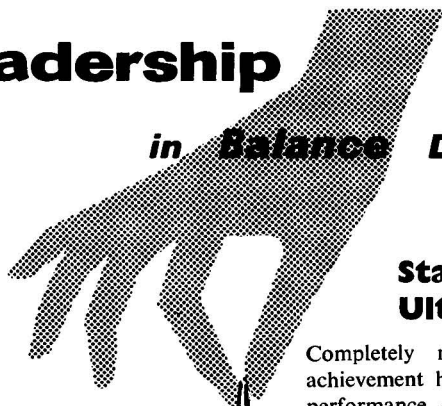
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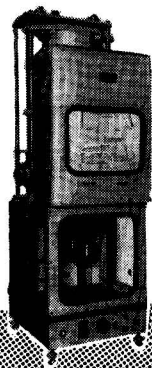
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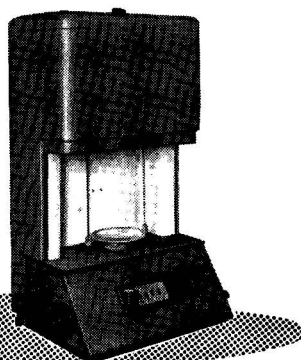
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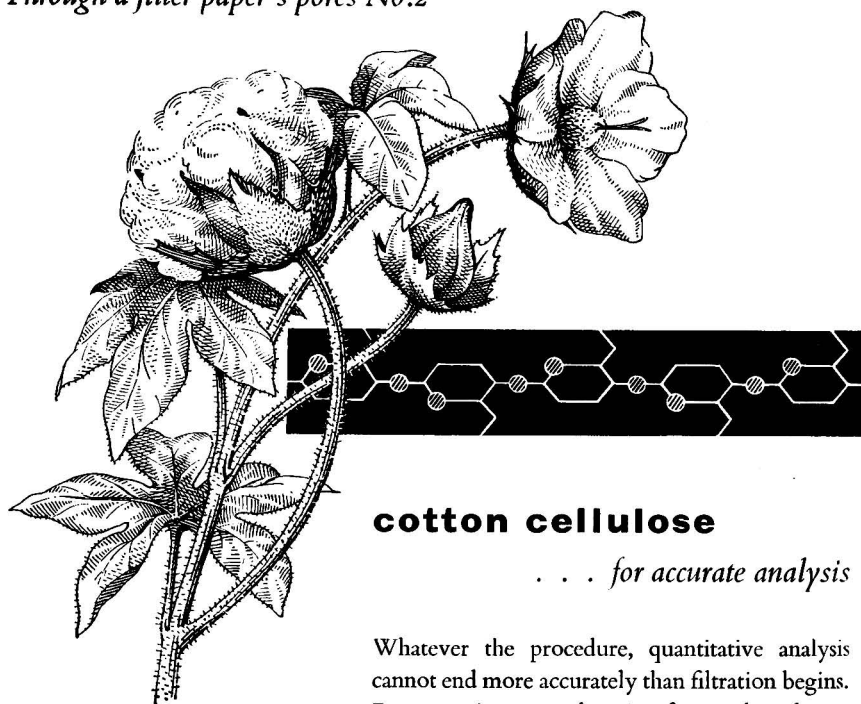
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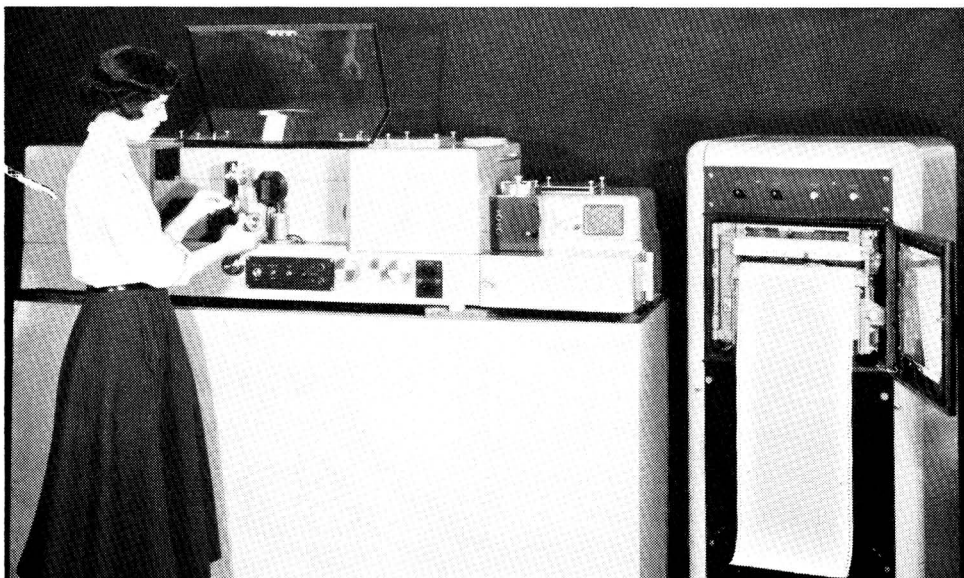
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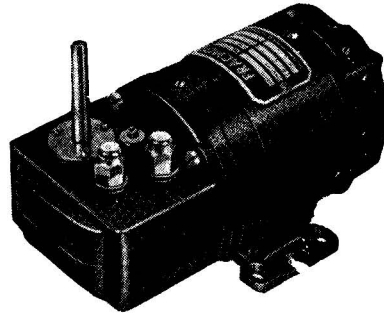
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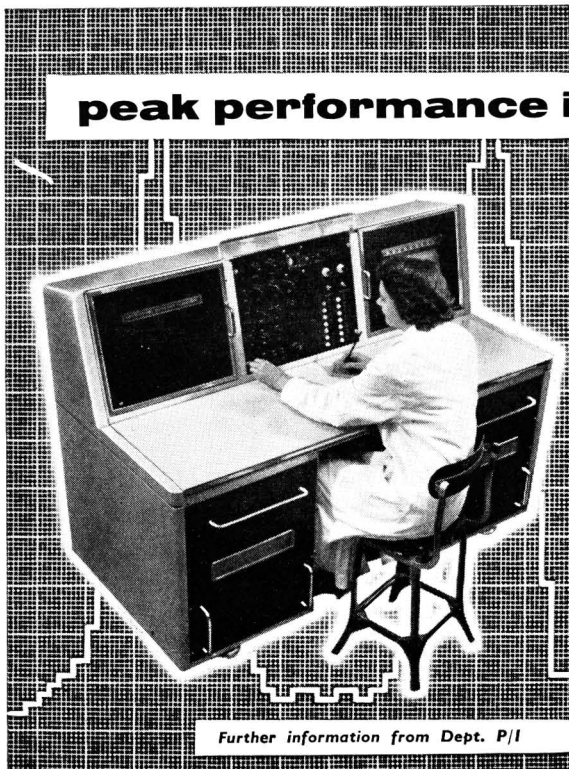
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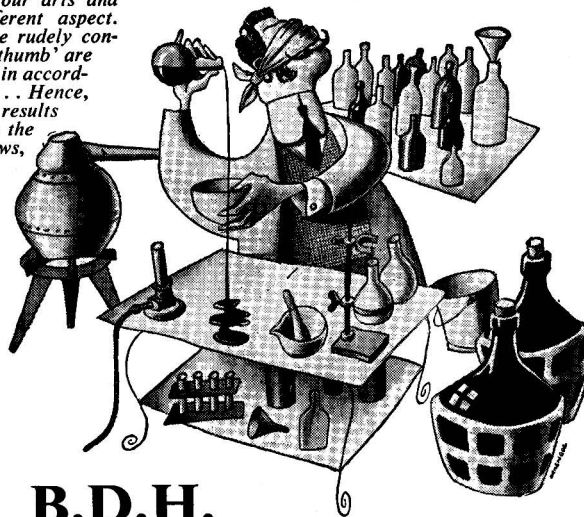
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