

# THE ANALYST

## PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

### GIFT TO THE SOCIETY

THE Council has the greatest pleasure in acknowledging the generous gift to the Society by Dr. G. Roche Lynch (Past President) of a long-case clock by Jonathan Loundes (Lowndes) of Pall Mall, *ca.* 1705. Dr. Roche Lynch has presented the clock to the Society for the Council Room, where it has now been installed.

### NEW MEMBERS

#### ORDINARY MEMBERS

Reginald Clifford Fawcett, M.Sc., Ph.D. (Manc.), A.R.I.C.; Paul Goudime, M.A. (Cantab.); Clarence Bertram Hackett; Alfred John Hookham; Clifford Raynor Johnson; Robert Julius Motz, Dipl.Ing.-Chem. (Vienna), A.R.I.C.; Derek Robbins, Grad.R.I.C.; Alfred John Shorter, M.Sc. (Birm.), M.S. (Illinois), A.R.I.C., M.Inst.F., F.Inst.Ceram.; Harold Vincent Street, B.Sc. (Birm.), M.I.Biol., F.R.I.C.; Reginald David Taylor, A.R.I.C.; Joseph Vincent Westwood, M.Sc. (Lond.), F.R.I.C.; Raymond Ernest Wilson, B.Sc. (Lond.), A.R.I.C.; Robert Wilson, B.Sc. (Edin.).

#### JUNIOR MEMBERS

Peter Adams, B.Sc. (Lond.); Ernest Draper; Michael Thomas Hall; Anthony John Harrison; John Coltherd Paxton, B.Sc. (Edin.).

#### DEATHS

WE record with regret the deaths of

Robert Luman Barnard  
Arthur Harvey  
Leslie Herbert Lampitt  
Herman Lee  
Albert Edward Parkes  
John W. Skirvin.

#### MIDLANDS SECTION

A SPECIAL General Meeting of the Section was held at 6.45 p.m. on Wednesday, April 10th, 1957, in the Mason Theatre, The University, Edmund Street, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.Inst.F., F.R.I.C., and an alteration was made to the Section Rules.

AN Ordinary Meeting of the Section was held at 7 p.m. on Wednesday, April 10th, 1957, in the Mason Theatre, The University, Edmund Street, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. R. Belcher, F.Inst.F., F.R.I.C.

The following paper was presented and discussed: "The Analytical Chemistry of Beryllium," by E. Booth.

## PHYSICAL METHODS GROUP

THE 58th Ordinary Meeting of the Group was held at 6.30 p.m. on Tuesday, May 21st, 1957, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the Chairman of the Group, Dr. J. E. Page, F.R.I.C.

The subject of the meeting was "Electrochemistry" and the following papers were presented and discussed: "Coulometric Titrations with an Integrated-current Source," by L. E. Smythe, M.Sc., Ph.D., A.R.I.C., F.R.A.C.I. (presented on his behalf by G. W. C. Milner, M.Sc., A.Inst.P., F.R.I.C.); "Pulse Polarography," by A. W. Gardner, B.Sc.

A commercial prototype of the coulometric titrimeter and a laboratory-built model of the pulse polarograph were demonstrated.

## Analytical Methods Committee

REPORT PREPARED BY THE PESTICIDES RESIDUES IN  
FOODSTUFFS SUB-COMMITTEE

### The Determination of Small Amounts of Total Organic Chlorine in Solvent Extracts of Vegetable Material

THE Analytical Methods Committee has received the following report from its Pesticides Residues in Foodstuffs Sub-Committee. The Report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

#### REPORT

In June, 1954, the Pesticides Residues in Foodstuffs Sub-Committee appointed a Working Party to carry out collaborative work on the determination of small amounts of chlorine in solvent extracts of foodstuffs for the purpose of detecting the presence of chlorinated hydrocarbons. This work had already been initiated by an Analytical Sub-Committee of the Fungicide and Insecticide Research Co-ordination Service of the Agricultural Research Council that had carried out much valuable, but unpublished, experimental work.

The members constituting the working party were nominated by the laboratories of Boots Pure Drug Co. Ltd., the Colonial Products Advisory Bureau, the Department of the Government Chemist and Dr. Bernard Dyer and Partners.

#### INTRODUCTION—

Consideration of the comprehensive investigations already undertaken by the A.R.C. Sub-Committee indicated that the cause of the wide variation in the results of their last recorded work on the determination of the organic-chlorine content of solvent extracts from grain impregnated with DDT and BHC could be either inefficient extraction from the grain or the method used for the determination of chlorine. The A.R.C. Sub-Committee could not decide which of these two factors was the cause of failure; accordingly, the working party of the Pesticides Residues in Foodstuffs Sub-Committee concluded that the immediate problem for investigation must be the method for determining known small amounts of organic chlorine compounds in organic solvents. The problem of the efficient solvent extraction of vegetable materials contaminated with halogenated hydrocarbons would then be a matter for subsequent investigation. It was further agreed, from examination of the available data, that the most promising procedure for the semi-micro determination of chlorine appeared to be that based on Stepanow's method,<sup>1</sup> *i.e.*, reduction by metallic sodium in *isopropanol*; accordingly, this procedure was adopted for the collaborative tests by the working party.

#### EXPERIMENTAL WORK—

The preliminary work of preparing the solvent extracts and the details of the analytical procedures was undertaken by the members from the Government Laboratory. First, green cabbages known to be uncontaminated by chlorinated hydrocarbons were extracted

with benzene to yield a heavily coloured extract. Since, however, benzene is an unsuitable solvent for the chromatographic separation included in the subsequent analytical procedure, this extract was evaporated to dryness and the residue dissolved in light petroleum.

This solution was then washed with water to remove water-soluble chloride and was divided into three portions. To two of the portions known amounts of DDT were added, and the chlorine was determined in all three. Samples of the three solutions (I, II and III) were distributed to the participating laboratories for chromatographic separation of the vegetable colouring matter and subsequent determination of the organic chlorine by both the mercuric oxycyanide method<sup>2,3,4</sup> and the turbidimetric method.

RESULTS OF COLLABORATIVE TESTS—

Results by the mercuric oxycyanide method were submitted by all four laboratories. Results by the turbidimetric method were submitted with confidence by two laboratories only. The fourth laboratory found this method unsatisfactory and did not submit any results. The collected results are shown in Table I.

TABLE I  
SUMMARY OF RESULTS FOR THE ORGANIC CHLORINE CONTENT OF A LIGHT PETROLEUM EXTRACT OF GREEN CABBAGE CONTAINING KNOWN AMOUNTS OF DDT

Laboratory	Method	Chlorine* in plant material (less blank)			Chlorine in blank, $\mu\text{g/g}$
		Solution I, $\mu\text{g/g}$	Solution II, $\mu\text{g/g}$	Solution III, $\mu\text{g/g}$	
A	Mercuric oxycyanide	3.7 3.4	17.1 18.25	} 0.1	{ 0.7 1.1
	Turbidimetric	3.8 4.1	16.55 19.6		
B	Mercuric oxycyanide	3.86	17.62	None	{ 0.86 1.23 1.4
	Turbidimetric	3.52	18.5	None	
C	Mercuric oxycyanide	8.3	17.9	4.3	4.5
D	Mercuric oxycyanide	3.0	16.8	None	{ 3.2 2.3
Chlorine added		3.65	18.3	None	—

\* All results are the mean of two or more determinations. Each figure for Laboratory A is the mean from two different operators.

CONCLUSION—

From the results of the collaborative investigation, the working party came to the conclusion that the method of chromatographic separation followed by determination of the chlorine by the mercuric oxycyanide procedure was satisfactory for determining small amounts of organic chlorine derived from DDT, but it was not known how far this method would be applicable to other chlorinated hydrocarbons.

Details of the recommended method are given in Appendix I.

Grateful appreciation is expressed by the working party for the valuable help given by Dr. A. J. Feuill of the Colonial Products Laboratory and by Mr. G. A. Sergeant of the Government Laboratory.

Appendix I

DETERMINATION OF TOTAL ORGANIC CHLORINE IN SOLVENT EXTRACTS OF VEGETABLE MATERIAL

NOTE—All reagents (including distilled water) and apparatus should be free from chloride, and care should be taken to prevent the access of chlorine or chlorine-containing compounds, e.g., hydrochloric acid, ammonium chloride or chloroform, from the atmosphere.

CHROMATOGRAPHIC SEPARATION OF VEGETABLE COLOURING MATTER

APPARATUS—

A glass tube, of about 17 mm internal diameter and 20 cm long, drawn out to give a narrow opening at one end.

## REAGENTS—

*Alumina*—For chromatographic analysis. This may contain a small amount of water, whereby its absorptive efficiency is considerably reduced. If so, the material should be dried at 200° to 300° C.

*Benzene*—“Crystallisable” grade.

*Light petroleum*—Analytical-reagent grade, boiling range 40° to 60° C. This must be free from aromatic hydrocarbons and chloride.

*Sodium sulphate, anhydrous*—Analytical-reagent grade.

## PROCEDURE—

Charge the tube with 8 g of alumina held in place by a wad of cotton-wool. Tap down the alumina to produce a level surface and then add a 1-inch layer of anhydrous sodium sulphate. Clamp the tube vertically. Pour in sufficient light petroleum to wet the column and then introduce the test solution, followed, at appropriate intervals, by four successive 10-ml washings of a mixture of four parts by volume of light petroleum and one part of benzene.

Evaporate the eluate, which should be colourless, to about 10 ml on a hot-plate, assisting the operation by directing on to the surface of the liquid a gentle stream of air that has been passed through a suitable desiccant, *e.g.*, silica gel, and then through a cotton-wool filter. The solution is then ready for reduction.

## STEPANOW SEMI-MICRO METHOD OF REDUCTION

## APPARATUS—

A 50-ml round-bottomed flask attached to a small reflux condenser by a ground joint.

## REAGENTS—

*isoPropanol*—Analytical-reagent grade, and a (1 + 1) aqueous dilution.

*Sodium*—Pellets in liquid paraffin and uniformly free from chloride. If such a grade of sodium is not obtainable from the suppliers, a suitable grade for this method may be produced from that normally supplied by the procedure given in Appendix III.

*Diethyl ether*—Tested for freedom from water-soluble chloride.

*Nitric acid, diluted (1 + 2)*—Analytical-reagent grade.

*Potassium hydroxide, 5 per cent. w/v*—Rinse sticks of the analytical-reagent grade solid with distilled water before dissolving.

*Hydrogen peroxide, 20-volume*—Analytical-reagent grade.

*Phenolphthalein indicator solution*—A 0.1 per cent. solution in 95 per cent. ethanol.

## PROCEDURE—

Transfer the solution prepared by the chromatographic separation to the dry 50-ml flask and evaporate just to dryness by immersing the flask in water at 40° C and blowing in a gentle current of dry, filtered air.

To the residue in the flask add 4 ml of *isopropanol* and approximately 0.3 g of sodium cut into several pieces. Attach the reflux condenser (dry) and boil for half an hour over a micro-burner (*e.g.*, a Bunsen burner from which the top has been unscrewed); then, while continuing the boiling, slowly add 2 ml of diluted *isopropanol* (1 + 1). When all the residual sodium has disappeared, discontinue heating and rinse down the condenser with about 5 ml of distilled water. Remove the flask, cool, add phenolphthalein indicator solution\* and acidify with diluted nitric acid (1 + 2). Rinse the contents of the flask into a small separating funnel to a total volume of about 25 ml and add 10 ml of diethyl ether. Shake the mixture well, allow it to stand and then run the aqueous layer into a 50-ml calibrated flask. Wash the ethereal layer with 10 ml of distilled water, and to the total aqueous extract in the flask add 5 drops of 20-volume hydrogen peroxide (to destroy any sulphide, see Note, p. 382), phenolphthalein indicator solution\* and 5 per cent. w/v potassium hydroxide solution until alkaline. Dilute the solution to 50 ml.

\* A modification of this procedure was used by one operator as follows: methyl red indicator was used instead of phenolphthalein when acidifying the solution after the treatment with sodium, and screened methyl red after the ether extraction.

## MERCURIC OXYCYANIDE DETERMINATION OF CHLORIDE

## REAGENTS—

*Sulphuric acid, 0.002 N or 0.004 N.*†

*Sulphuric acid, approximately 0.01 N.*

*Potassium hydroxide solution, approximately 0.01 N.*

*Screened methyl red indicator solution*—Mix equal volumes of (a) 0.125 g of methyl red in 50 ml of 90 per cent. ethanol and (b) 0.083 g of methylene blue in 50 ml of 90 per cent. ethanol.

*Mercuric oxycyanide reagent*—Dissolve 4 g of mercuric oxycyanide as completely as possible in 100 ml of distilled water, with stirring and moderate heating. Filter the solution through a close-grained filter-paper, cool, add a few drops of screened methyl red indicator solution and then add 0.01 N sulphuric acid until the solution assumes a grey tint.

*Standard potassium chloride solution, 0.0002 N.*

## PROCEDURE—

Transfer a suitable aliquot (say, 25 ml) of the 50 ml of solution from the Stepanow reduction to a small evaporating basin and add almost sufficient 0.01 N sulphuric acid to decolourise the phenolphthalein. Evaporate the solution to dryness on a steam-bath or under an infra-red lamp, dissolve the residue in distilled water and rinse it into a 25-ml tall beaker. Add 2 drops of screened methyl red indicator solution, heat to boiling and add 0.01 N sulphuric acid until the solution is just acid. Boil to remove carbon dioxide and continue boiling to reduce the volume to about 5 ml.\*

Cool the solution and make it just alkaline with 0.01 N potassium hydroxide. Titrate to a faint violet-grey tint with 0.002 N or 0.004 N† sulphuric acid; then add 0.5 ml of mercuric oxycyanide reagent and titrate to the original tint with the 0.002 N acid from a 5-ml burette.

## BLANK—

Take the whole of the final solution from the blank Stepanow reduction and proceed as described above. The final blank titration should be carried out on the same volume of solution as is titrated in the test.

## STANDARDISATION OF THE SULPHURIC ACID WITH RESPECT TO CHLORINE—

Place 0, 5, 10, 20, 30, 40 and 50-ml portions of 0.0002 N potassium chloride in evaporating basins. To each, add 1 drop of 0.01 N potassium hydroxide and evaporate to dryness, and then proceed as directed above.

Titration values corrected for the blank (on the 50 ml from the blank Stepanow reduction) should, when plotted against volumes of standard chloride, show a very nearly linear relationship. This linear relationship does not hold so closely for the higher titration values if much less mercuric oxycyanide reagent, e.g., 0.15 ml, is added or if a more dilute acid is used.

## CALCULATION—

If  $T$  ml of test solution require  $S$  ml of acid (after deducting  $T/50$  of the volume of acid required by the whole of the blank) and  $S$  ml of the acid are, from the standardisation graph, equivalent to  $A$  ml of 0.0002 N potassium chloride,

then the whole sample contains  $\frac{50 \times A \times 35.5 \times 0.0002 \times 10^6}{T \times 1000}$   $\mu\text{g}$  of chlorine.

For a 25-g sample, the DDT content will be

$$= \frac{50 \times A \times 35.5 \times 0.0002 \times 10^6 \times 2}{T \times 1000 \times 25} \mu\text{g per g or p.p.m.}$$

$$= \frac{28.4 \times A}{T} \mu\text{g per g or p.p.m.}$$

\* When evaporating the solution in the 25-ml beaker before the titration, some form of boiling-rod should be used to promote uniform boiling. Especially useful for this purpose is a device consisting of a  $\frac{1}{4}$ -inch square of  $\frac{3}{8}$ -inch polytetrafluoroethylene sheet perforated and pushed on to the end of a 3-inch glass rod, the tip of which has been drawn out and finally melted to form a retaining knob.

† For the titration, 0.004 N sulphuric acid may be preferred to 0.002 N. This reduces the dilution on titration, especially for the higher titration values and thereby sharpens the end-point.

NOTE—The addition of hydrogen peroxide may be omitted in the reduction stage, since any sulphide formed should be decomposed on boiling the acidified solution before titration in the mercuric oxycyanide determination.

## Appendix II

### ALTERNATIVE PROCEDURE FOR DETERMINING CHLORINE BY THE MERCURIC OXYCYANIDE METHOD

#### REAGENTS—

*Sulphuric acid, approximately 3 N.*

*Sulphuric acid, approximately 0.01 N.*

*Sulphuric acid, 0.0005 N.*

*Diethyl ether*—Tested for freedom from water-soluble chlorides.

*Hydrogen peroxide, 20-volume*—Analytical-reagent grade.

*Mercuric oxycyanide reagent*—As described in Appendix I.

*Methyl red indicator solution*—A 0.04 per cent. aqueous solution.

#### PROCEDURE—

Carry out the chromatographic separation and the Stepanow reduction as far as the elimination of excess of sodium. Acidify the resulting solution to methyl red with 3 *N* sulphuric acid and extract with diethyl ether. Run off the aqueous phase into the original flask, wash the ethereal layer with 10 ml of water and add it to the main aqueous bulk. Add 5 drops of 20-volume hydrogen peroxide (see Note at end of Appendix I, above), make the solution just alkaline, boil, cool, neutralise with 0.01 *N* sulphuric acid and dilute to 50 ml.

Transfer a 5-ml or 10-ml aliquot to a 50-ml narrow-necked conical flask and add 4 drops of methyl red indicator solution, followed by a slight excess of 0.0005 *N* sulphuric acid. Boil for 2 minutes to remove carbon dioxide and transfer the solution to a 25-ml wide-necked flask with distilled water free from carbon dioxide. Into another similar flask put the same quantity of distilled water free from carbon dioxide and of methyl red indicator solution. Adjust the blank solution with 0.0005 *N* sulphuric acid until slightly pink. Adjust the test solution to the same tint.

Add 2 ml of the neutral 2 per cent. solution of mercuric oxycyanide to each ampoule and titrate the liberated sodium hydroxide with 0.0005 *N* sulphuric acid to the original tint, as shown by the blank, which should be diluted with distilled water free from carbon dioxide to the same volume as the titrated test solution.

## Appendix III

### PREPARATION OF CHLORIDE-FREE SODIUM

Although the total chloride content of a sample of sodium may be small, the distribution of the chloride appears to be irregular, so that comparatively large amounts may be contained in the small portions used in this determination. By separating, as far as possible, the clean metal from the dross, a satisfactory grade of sodium can be obtained. The following procedure is recommended—

Take about four pellets of sodium (9 to 12 g) and melt them in a 6-inch × 1-inch Pyrex-glass test-tube under a few millilitres of liquid paraffin, B.P. Stir vigorously with a glass rod to separate dross and heat fairly strongly to help coagulate globules of sodium. Introduce into the molten sodium a heated glass tube about 1 cm in diameter, narrowed at the lower end to a jet about 1 mm in diameter and constricted at the top to take a length of rubber tubing. Draw up a quantity of clean sodium and transfer it to a clean test-tube containing liquid paraffin.

To get the cleaned sodium in a convenient form, re-melt it, insert a piece of clean 5-mm bore glass tubing wetted internally with liquid paraffin and draw up about 2 inches of the molten metal, which, after cooling and solidifying, can be extruded as required with the aid of a glass rod.

#### REFERENCES

1. Klein, A. K., and Wichmann, H. J., *J. Ass. Off. Agric. Chem.*, 1946, **29**, 191.
2. Vieböck, F., *Ber.*, 1932, **65**, 496.
3. Ingram, G., *Analyst*, 1944, **69**, 265.
4. Belcher, R., Macdonald, A. M. G., and Nutten, A. J., *Microchem. Acta*, 1954, 104.

## Sodium Carbonate as a Volumetric Standard\*

By W. C. EASTERBROOK

Sodium carbonate has frequently been proposed as a working standard for acidimetry, but objections have been made to its use on the grounds of alleged lack of purity and stability. In spite of this, sodium carbonate prepared by heating sodium sesquicarbonate is used by Imperial Chemical Industries Ltd. Recent experiments carried out on a thermobalance have confirmed that sodium carbonate prepared by heating sodium sesquicarbonate at 270° C is perfectly stable over long periods at this temperature.

Although the preparation of sodium carbonate and the method of referring it to pure silver used as the ultimate volumetric standard have been described, no account has ever been given of the work that first led to the adoption of sodium carbonate as a working standard for Imperial Chemical Industries Ltd. or of the preparation and assay of subsequent batches of the material. This work is now described and includes the assay of materials containing 100.023, 100.013 and 100.008 per cent. of sodium carbonate. It establishes beyond doubt the purity and stability, and hence the suitability as an acidimetric standard, of properly prepared sodium carbonate.

A recent spectrographic analysis of the ultimate standard silver, to which the sodium carbonate was referred, has given a value of rather better than 99.998 per cent. of silver.

SINCE early in the nineteenth century, sodium carbonate has been recommended as a volumetric standard and, in spite of alleged lack of purity and stability when prepared by different methods, it is still widely approved<sup>1</sup> for this purpose. The numerous papers published on the subject contain statements that appear to be contradictory, and these have been responsible for much of the uncertainty existing on the reliability of sodium carbonate as a reference standard in acidimetry.

Amongst the chief difficulties reported in the literature have been the removal of residual water,<sup>2,3</sup> the apparent instability on heating,<sup>4,5</sup> the high solubility in water, which defeats easy purification, and the hygroscopic nature of the anhydrous carbonate.<sup>6,7</sup> It would seem that these objections may be associated with too severe or ill-defined experimental conditions, or both.

Sodium hydrogen carbonate of high purity has been largely adopted as the source of anhydrous carbonate, because it is simply converted at relatively low temperatures. This procedure was recommended by Gay-Lussac and also by Lunge,<sup>8,9,10</sup> who showed that sodium carbonate obtained in this way was stable for long periods when heated in the region of 300° C, and his work is confirmed by the experimental work reported in this paper. There are, however, widely differing views in the literature, not only on the best temperature of conversion to the normal carbonate, but also on the composition of the final product, which is alleged to contain oxide or hydroxide.<sup>8,9,10,11,12,13,14</sup> The temperature recommended for the conversion of sodium hydrogen carbonate to sodium carbonate varies over a wide range, namely from 102° to 450° C.<sup>14</sup> At temperatures below 200° C some workers claim that the decomposition is incomplete, whereas at temperatures of 380° C or over it would appear that decomposition proceeds beyond the stage of normal carbonate, to carbon dioxide, water and sodium oxide or hydroxide. On these points there is some evidence to show that at lower temperatures complete conversion from the sesquicarbonate or hydrogen carbonate to the normal carbonate is not so much a function of the temperature as of the duration of the heating period; for instance, both salts are transformed to the normal carbonate by exposure in a boiling-water oven for a period of about 50 hours.

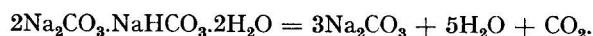
It would be difficult to reconcile all the conflicting views on this subject; however, the experimental work summarised below should help to dispel some of the many doubts that still exist in the minds of those who by tradition rely on sodium carbonate as a reference standard.

\* Presented at the XVth International Congress on Pure and Applied Chemistry (Analytical Chemistry), Lisbon, September 8th to 16th, 1956.

THERMAL STABILITY AND HYGROSCOPICITY OF SODIUM CARBONATE DERIVED  
FROM SODIUM SESQUICARBONATE

Sodium hydrogen carbonate is readily converted to sodium sesquicarbonate,<sup>1,15</sup> which has obvious advantages as a starting material in preparing sodium carbonate. First, it is possible in this conversion to remove mechanical and other impurities and, secondly, the sodium sesquicarbonate so obtained is easier to handle than the finely divided sodium hydrogen carbonate from which it is derived.

The loss in weight of sodium sesquicarbonate on sustained heating is not a reliable criterion on which to judge purity, because of the ease with which the material dissociates at relatively low temperatures. The chief factor of concern in the present instance was the stability of the sodium carbonate derived as a residue on heating sodium sesquicarbonate under defined and controlled temperature conditions. The constancy in weight of the sodium carbonate was obviously one of the simplest means of measuring this stability. Simple experiments were carried out by heating the sodium sesquicarbonate in platinum or silver capsules in an electrically heated air-oven at 270° C. The decomposition is indicated by the equation—



The progressive change in weight and percentage loss in terms of time that sodium sesquicarbonate and sodium hydrogen carbonate undergo when heated to 270° C are given in Table I.

TABLE I

STABILITY OF SODIUM CARBONATE OBTAINED BY HEATING SODIUM SESQUICARBONATE  
AND SODIUM HYDROGEN CARBONATE AT 270° C

Time of heating, hours	Sodium sesquicarbonate				Sodium hydrogen carbonate			
	Weight of residue in test 1, g	Loss in weight in test 1, %	Weight of residue in test 2, g	Loss in weight in test 2, %	Weight of residue in test 1, g	Loss in weight in test 1, %	Weight of residue in test 2, g	Loss in weight in test 2, %
2	10.5158	29.89	10.5151	29.90	9.4745	36.85	9.4729	36.86
6	10.5169	29.88	10.5143	29.91	9.4750	36.85	9.4736	36.86
10	10.5173	29.88	10.5149	29.90	9.4765	36.84	9.4752	36.84
14	10.5157	29.89	10.5145	29.90	9.4750	36.85	9.4741	36.85
30	10.5152	29.89	10.5147	29.90	9.4742	36.85	9.4737	36.85
46	10.5161	29.89	10.5133	29.91	9.4743	36.85	9.4732	36.86
Weight of sample	14.9983		15.0001	Theory 29.66	15.0035		15.0030	Theory 36.91

The losses in weight suffered by sodium hydrogen carbonate and sodium sesquicarbonate, respectively, remain constant during the heating time of from 2 to 46 hours. Although reasonable constancy in weight was found after 2 hours, small fluctuations that would appear to be of little practical importance persisted throughout the tests.

It seemed reasonable, however, to carry out tests of a more critical character with the aid of a thermal balance, so that a continuous instead of an intermittent record of the weight could be obtained. The results obtained with sodium sesquicarbonate are shown in Fig. 1, which shows that dissociation with loss of carbon dioxide and water was virtually complete at a temperature of 210° C and within 2 hours of the commencement of heating. Thereafter, the chart readings indicate no detectable change. This is shown in Figs. 2 and 3 of the continuous record, that is, after exposure at 270° C for 6 to 8 hours and for 19 hours. The operating temperature of the heating chamber was then increased to 340° C. In the intervening periods no appreciable change in weight was apparent.

The stability test was repeated with sodium sesquicarbonate that had already been converted to normal carbonate by exposure in an electrically heated air-oven at 270° C for 18 hours. By this means it was possible to increase the size of the sample under test from 2 to 5 g. The results obtained are shown in Fig. 4.

Figs. 4 and 5 represent 6 to 8 hours and 18 to 20 hours, respectively, of additional heating, and again they show no significant change in weight. The temperature of the heating chamber was finally raised to 340° C. At that temperature an increase of 1 mg in the weight was recorded; this is attributed to the change in buoyancy with increase of temperature. A



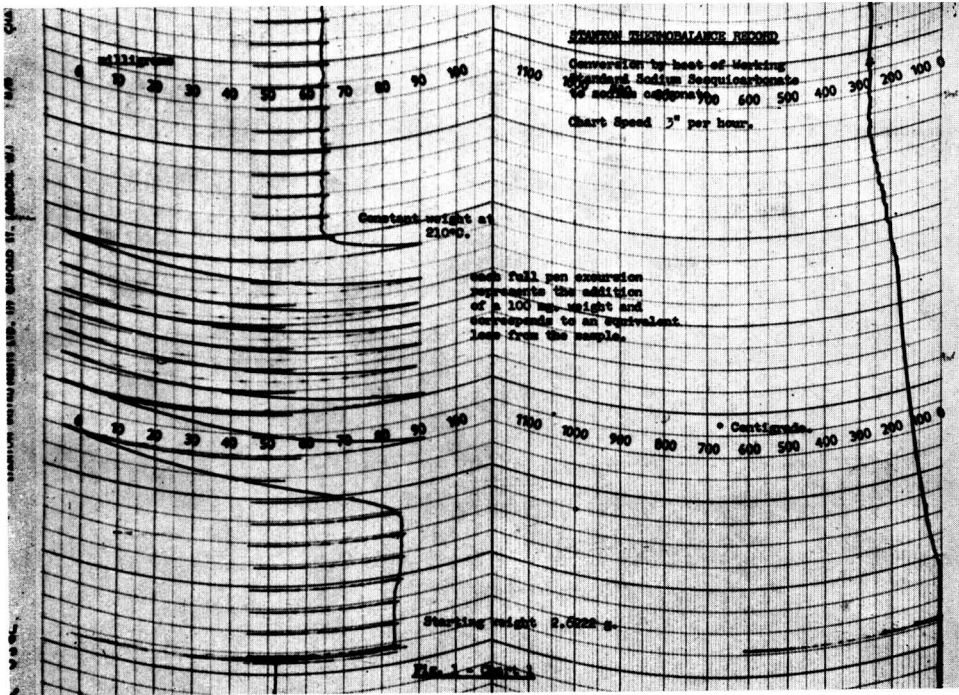


Fig. 1. Chart 1

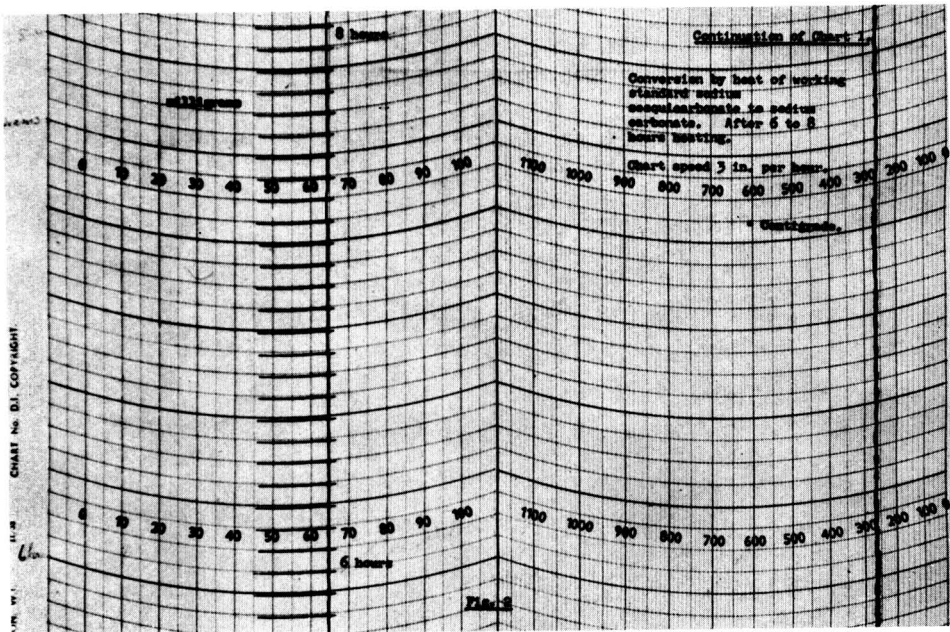


Fig. 2. Continuation of Chart 1

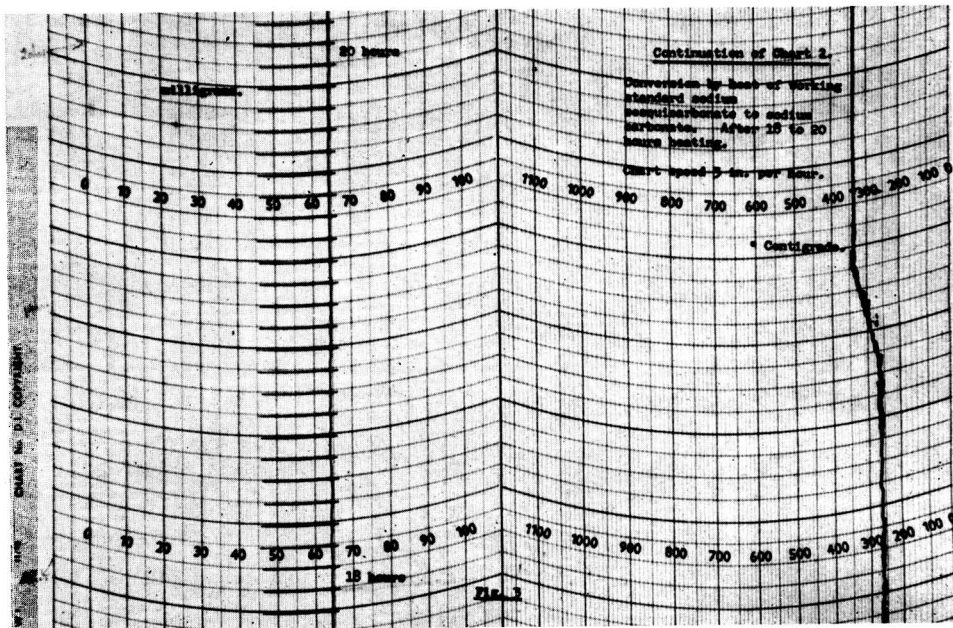


Fig. 3. Continuation of Chart 1

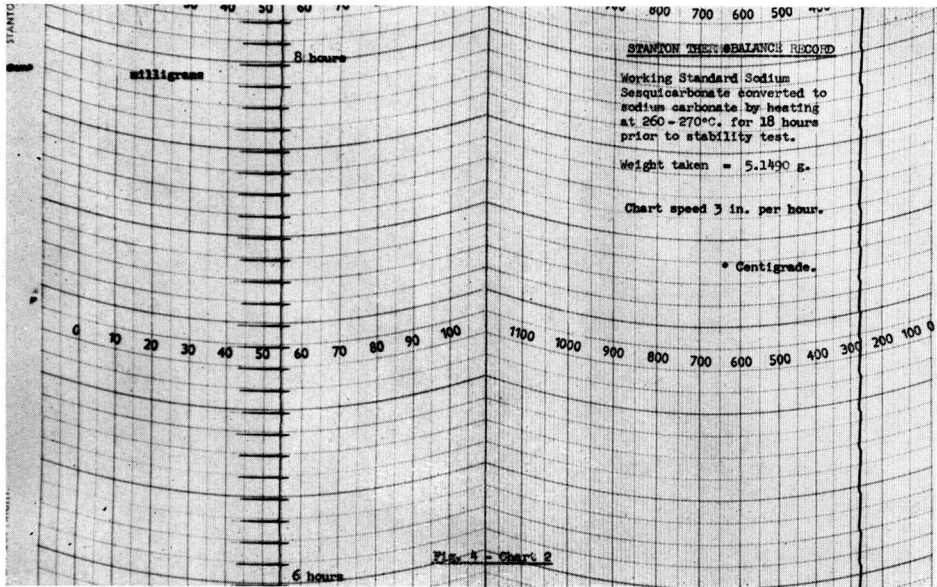


Fig. 4. Chart 2

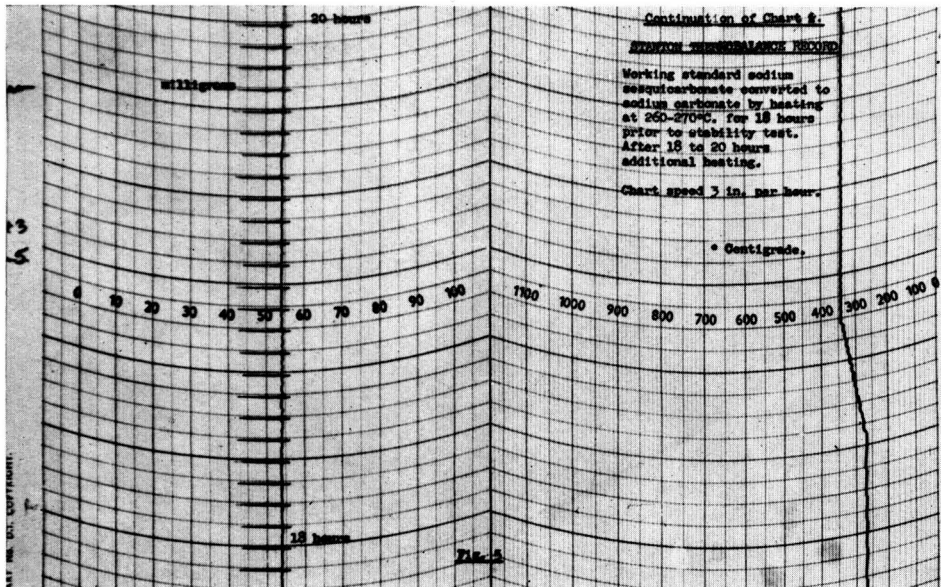


Fig. 5. Continuation of Chart 2

blank test made under the same conditions showed the same response. The maximum variation of the blank was estimated to be about  $\pm 0.25$  mg and is attributed chiefly to inherent variability of the instrument.

It is concluded from these tests that sodium carbonate obtained from sodium sesquicarbonate by heating under controlled conditions at 270° C for a period of 2 to 20 hours is completely stable at that temperature.

The sodium carbonate prepared in this way is very slightly hygroscopic at ordinary temperatures and under ordinary conditions. The magnitude of any error that might arise from this cause was examined in the following way—

Weigh the quantity of working standard into a silver or platinum crucible, and heat it to 270°  $\pm$  10° C in an electrically heated oven until it is constant in weight. Transfer the crucible to a stoppered weighing bottle of suitable size, close the bottle and place it in a desiccator to cool thoroughly. Transfer the bottle to the balance case, momentarily release the stopper of the weighing bottle and, after an interval of 30 minutes, weigh it accurately. Empty the contents of the crucible into a dry 500-ml conical flask, placing the crucible well inside the neck of the flask in order to avoid loss. Replace the crucible immediately in the bottle, transfer the whole to the balance case and weigh it after an interval as before. When the weight of the weighing bottle with contents has been found to be constant, the time necessary to transfer the sodium carbonate to the conical flask was estimated at about 30 seconds. The increase in weight sustained by the weighing bottle with capsule and sodium carbonate was in the interval about 30  $\mu$ g, so that any uptake of moisture by the empty capsule and weighing bottle would be a fraction of this weight.

In an experiment 4.5 g of working-standard sodium sesquicarbonate were heated overnight in a silver capsule at 270° C. The capsule was then cooled in a weighing bottle as described above. The results are shown in Table II. For the first hour the increase in weight is fairly constant at about 0.00003 g per 30 seconds; after this the rate of increase falls off. The procedure adopted in weighing the sodium carbonate precludes any increase in weight that could significantly affect the analytical result.

TABLE II

HYGROSCOPICITY OF FRESHLY HEATED WORKING-STANDARD SODIUM CARBONATE PREPARED BY HEATING SODIUM SESQUICARBONATE

Test No.	Details of test	Weight, g	Remarks
1	Weighing bottle with capsule and carbonate were weighed	54.96112	Weighing at 5-minute intervals
2		54.96118	
3		54.96117	
			Initial weighing after—
4	The stopper of the weighing bottle was removed and the weighings were continued	54.96117	$\frac{1}{2}$ minute
5		54.96120	1 minute
6		54.96123	1½ minutes
7		54.96128	2 minutes
8		54.96132	2½ minutes
9		54.96137	3 minutes
10		54.96166	10 minutes
11		54.96197	15 minutes
12		54.9643	1 hour
13		54.9657	2 hours
14		54.9658	3 hours
15		54.9664	4½ hours

SCHEME OF STANDARDISATION OF VOLUMETRIC SOLUTIONS

SODIUM CARBONATE AS A REFERENCE STANDARD IN ACIDIMETRY—

Unfortunately, there is insufficient systematic investigational work in the literature to justify reasonably the basis of a general scheme of standardisation with reference and ultimate standards, although such a scheme was recommended by Wagner at the Fifth International Congress in 1903. He suggested that reference and ultimate standards should be examined in two or more different ways, for example, acidimetrically and oxidimetrically. The success of such a plan would necessarily depend on the ultimate standard being of high

purity. This principle was in effect put into practice in 1912 by Dr. E. G. Beckett in the Research Laboratories of Nobel's Explosives Co. Ltd., when the initial part of the Imperial Chemical Industries Ltd. scheme of standardisation was first evolved. It was then decided that the substance that best fulfils the exacting and critical properties of an ultimate standard is silver. However, it is admitted that silver has certain disadvantages, namely it cannot be used directly for the standardisation of acids, except hydrochloric acid, and even in this instance the standardisation would only be correct if the acid were entirely free from its salts and from other acids. Further, it cannot be used directly for the standardisation of oxidising or reducing substances. To overcome these disadvantages, it was decided to employ "working standards" to be used for the standardisation of laboratory solutions direct.

As a working standard for acids and alkalis, pure sodium carbonate was selected and its strength was determined by titration with pure hydrochloric acid, the strength of which had been ascertained by comparison with the ultimate standard silver.

#### SELECTION OF SODIUM CARBONATE AS WORKING STANDARD—

At this stage it had been decided to use sodium sesquicarbonate as the source of anhydrous carbonate and two sources were available for its preparation, namely,

- (a) from pure sodium hydrogen carbonate ("sodium carbonate 1"),
- (b) from commercially pure anhydrous sodium carbonate ("sodium carbonate 2").

*Preparation of sodium carbonate 1*—The purest grade of sodium hydrogen carbonate available was added in small quantities to water at 86° C in a resistance-glass flask until no more would dissolve. The solution was then rapidly filtered and cooled thoroughly and the mother-liquor was poured off. The crystals of sodium sesquicarbonate were ground in a mortar and sucked dry in a Hirsch funnel. The moist powder was dried in a porcelain basin and heated on a water bath until the powder had a perfectly dry appearance. It was powdered again, well mixed and sealed in resistance-glass ampoules.

*Preparation of sodium carbonate 2*—An alternative method for the preparation of sodium carbonate from pure anhydrous carbonate was also examined. After recrystallisation, the salt was dissolved in water and purified carbon dioxide gas was passed into the solution at 0° C until no further gas was absorbed. The sodium hydrogen carbonate was isolated and it was then converted to the sodium sesquicarbonate by the method referred to above.

The purity of the two sodium sesquicarbonates and the hydrogen carbonate and anhydrous carbonate from which they were derived, after heating to 270° C, was determined by reference to ultimate standard silver. The true weights of sodium carbonate and silver were obtained by using a high-precision balance with a sensitivity of  $\pm 0.01$  mg. Weighings were made by the method of substitution with weights recently calibrated to class "A" accuracy on a mass basis at the National Physical Laboratory. The results are given in Table III.

TABLE III

PURITY OF SODIUM CARBONATES OBTAINED THROUGH SODIUM SESQUICARBONATE FROM SODIUM HYDROGEN CARBONATE AND SODIUM CARBONATE BY EVALUATION WITH ULTIMATE STANDARD SILVER

Description of sample	Purity of sodium carbonate after heating to 270° C until constant in weight, %
Sodium hydrogen carbonate used in the preparation of sodium sesquicarbonate	99.988
Sodium carbonate 1 derived from sodium sesquicarbonate .. .. .	100.000
	100.003
Sodium carbonate (anhydrous) used in preparation of sodium sesquicarbonate	99.996
odium carbonate 2—	
(a) derived from sodium sesquicarbonate .. .. .	99.976
(b) derived from sodium sesquicarbonate after recrystallisation .. .. .	99.974
(c) derived from sodium sesquicarbonate mother-liquor .. .. .	99.972

The results in Table III show that—

- (a) sodium carbonate 1 (sesquicarbonate) and the sodium hydrogen carbonate from which it was derived gave carbonates of high purity, and

(b) sodium carbonate 2 (sesquicarbonate) prepared from pure anhydrous sodium carbonate was slightly less pure than the original anhydrous carbonate from which it was derived. On account of this slight fall in purity, the sodium carbonate (sesquicarbonate) was recrystallised and both crystals and residue from the mother-liquor were tested as described above, but the results failed to show an improvement. This may be explained by small amounts of silica dissolved from the glass vessels used in recrystallisation.

The experiments, therefore, favoured the method in which high-grade sodium hydrogen carbonate was further purified and transformed to sodium sesquicarbonate before conversion to normal carbonate by heating to 270° C, and this method was finally adopted in the preparation of working-standard sodium carbonate.

During the preparation of a new lot of sodium sesquicarbonate the individual batches, the blended batches and the bottled material were exhaustively tested by weight titrations with *N* hydrochloric acid to ensure homogeneity.

In order to assess the purity of the sodium carbonate derived from the heat treatment of sodium sesquicarbonate at 270° C, pure silver was used as the ultimate standard. This procedure has been described in detail in the literature.<sup>1</sup> Briefly, it involves the weight titration of working-standard sodium carbonate with *N* hydrochloric acid previously standardised gravimetrically against the ultimate standard silver. This method has been employed for the evaluation of several lots of sodium carbonate prepared from different batches of sodium sesquicarbonate. The results of the evaluations are shown in Tables IV and V.

TABLE IV  
PURITY OF WORKING-STANDARD SODIUM CARBONATE: SERIES I

(a) *Determination of the ratio of silver to N hydrochloric acid by using ultimate standard silver and chemically pure silver, precipitants being 0.1 N—*

Expt. No.	True weight of silver required by <i>N</i> HCl, g	True weight of <i>N</i> HCl, g	Weight of silver equal to 100 g of <i>N</i> HCl, g	Silver used
5	9.80898	92.2569	10.6322	Ultimate standard
6	9.72351	91.4705	10.6302	Ultimate standard
7	8.10283	76.2103	10.6322	Chemically pure. Guaranteed minimum purity 99.99 per cent.
			Mean = 10.6315	

(b) *Determination of the ratio of sodium carbonate to N hydrochloric acid and purity of sodium carbonate—*

Expt. No.	True weight of Na <sub>2</sub> CO <sub>3</sub> , g	True weight of <i>N</i> HCl required by Na <sub>2</sub> CO <sub>3</sub> , g	Weight of Na <sub>2</sub> CO <sub>3</sub> equal to 100 g of <i>N</i> HCl, g	Mean weight of silver equal to 100 g of <i>N</i> HCl, g	Weight of Na <sub>2</sub> CO <sub>3</sub> equivalent to 107.88 g of silver, g	Equivalent weight of Na <sub>2</sub> CO <sub>3</sub> from International Atomic Weights (1925)	Purity of Na <sub>2</sub> CO <sub>3</sub> , %
1	3.63071	69.5332	5.22154	10.6315	52.984(0)	52.997	100.025
2	3.68262	70.5230	5.22187	10.6315	52.987(4)	52.997	100.018
3	3.69363	70.7376	5.22159	10.6315	52.984(6)	52.997	100.024
4	3.64518	69.8081	5.22171	10.6315	52.985(8)	52.997	100.021
8	5.25565	100.6529	5.22155	10.6315	52.984(1)	52.997	100.024
9	5.24120	100.3753	5.22170	10.6315	52.985(7)	52.997	100.021
10	5.25910	100.7198	5.22152	10.6315	52.983(8)	52.997	100.025
						Mean = 100.023	

From time to time during the interval covering the period of the experiments involving the determination of the actual sodium carbonate present, the standard hydrochloric acid was checked against the silver standard and the results given in the Tables show that no change occurred. The experiments described in Table IV were carried out with 0.1 *N* reagents, whereas those in Table V were obtained with reagents of normal strength. This was done in order to look for the possibility of adsorption of silver nitrate by silver chloride during the standardisation of the hydrochloric acid. The procedures recommended by

Richards and Wells<sup>16</sup> for dilution, order of addition of precipitants and so on were followed throughout this work. Comparison of the results shown in Tables IV and V indicates that there is no evidence that the results were affected by adsorption of silver nitrate. Table V also shows that there is no evidence of difference in the strength of hydrochloric acid resulting from storage in wax-lined containers or resistance-glass bottles.

TABLE V

## PURITY OF WORKING-STANDARD SODIUM CARBONATE: SERIES 2

(a) *Determination of the ratio of silver to N hydrochloric acid by using chemically pure silver, precipitants being N—*

Expt. No.	True weight of silver required by N HCl, g	True weight of N HCl, g	Weight of silver equal to 100 g of N HCl, g
11	7.93567	73.52884	10.7926
12	8.07762	74.83967	10.7932
13	8.23127	76.26780	10.7926
14	8.28278	76.74637	10.7924

Mean = 10.7927

(b) *Determination of the ratio of sodium carbonate to N hydrochloric acid and purity of sodium carbonate—*

Expt. No.	True weight of Na <sub>2</sub> CO <sub>3</sub> , g	True weight of N HCl required by Na <sub>2</sub> CO <sub>3</sub> , g	Weight of Na <sub>2</sub> CO <sub>3</sub> equal to 100 g of N HCl, g	Mean weight of silver equal to 100 g of N HCl, g	Weight of Na <sub>2</sub> CO <sub>3</sub> equivalent to 107.88 g of silver, g	Equivalent weight of Na <sub>2</sub> CO <sub>3</sub> from International Atomic Weights (1925)	Purity of Na <sub>2</sub> CO <sub>3</sub> , %
15	5.23072	98.67292	5.30107	10.7927	52.987(6)	52.997	100.018
16	5.23038	98.65911	5.30148	10.7927	52.991(7)	52.997	100.010
17	5.22948	98.64379	5.30138	10.7927	52.990(7)	52.997	100.012
18	5.22374	98.72326	5.30143	10.7927	52.991(2)	52.997	100.011

Mean = 100.013

In experiments No. 11, 12, 15 and 16 the acid was stored in wax-lined bottles.

In experiments No. 13, 14, 17 and 18 the acid was stored in resistance-glass bottles.

TABLE VI

## PURITY OF WORKING-STANDARD SODIUM CARBONATE: SERIES 3

(a) *Determination of the ratio of silver to N hydrochloric acid by using ultimate standard silver—*

Expt. No.	True weight of silver required by N HCl, g	True weight of N HCl, g	Weight of silver equal to 100 g of N HCl, g
19	9.85422	92.0528	10.7050
20	9.83063	91.8282	10.7055
21	9.94792	92.9289	10.7049

Mean = 10.7051

(b) *Determination of the ratio of sodium carbonate to N hydrochloric acid and purity of sodium carbonate—*

Expt. No.	True weight of Na <sub>2</sub> CO <sub>3</sub> , g	True weight of N HCl required by Na <sub>2</sub> CO <sub>3</sub> , g	Weight of Na <sub>2</sub> CO <sub>3</sub> equal to 100 g of N HCl, g	Mean weight of silver equal to 100 g of N HCl, g	Weight of Na <sub>2</sub> CO <sub>3</sub> equivalent to 107.88 g of silver, g	Equivalent weight of Na <sub>2</sub> CO <sub>3</sub> from International Atomic Weights (1925)	Purity of Na <sub>2</sub> CO <sub>3</sub> , %
22	3.54248	67.3714	5.25814	10.7051	52.988(6)	52.997	100.016
23	3.49702	66.5003	5.25865	10.7051	52.993(7)	52.997	100.006
24	3.53805	67.2790	5.25879	10.7051	52.995(2)	52.997	100.004
25	3.56779	67.8450	5.25874	10.7051	52.994(6)	52.997	100.005

Mean = 100.008

The mean values of the purity of the sodium carbonate from Tables IV and V are  $100.023 \pm 0.003$  and  $100.013 \pm 0.005$  per cent., respectively. This leads to the conclusion that some oxide or hydroxide is formed during the decomposition<sup>17</sup> of the sodium sesquicarbonate, but the amount is not sufficiently large to make any significant difference when the material is used as a standard. As Table I and the charts on thermal stability show that prolonged heating of sodium carbonate at 270° C does not result in any appreciable decomposition, it seems reasonable to conclude that the slight decomposition that occurs (accounting for the slightly high results, see Tables IV (a) and (b)) takes place during the decomposition of the sesquicarbonate (or hydrogen carbonate), oxide or hydroxide only being produced while moisture is being lost. The dry sodium carbonate is then completely stable to heat at 270° C.

The results of tests for the purity of a further lot of sodium carbonate are shown in Table VI.

For effective comparison, the results in Table VI have been calculated with the same atomic weights (1925) as those of the earlier figures. If the atomic weight of carbon, however, is taken as 12.01, *i.e.*, the 1954 value, the level of the purity of sodium carbonate would be raised by 0.009 per cent., and the magnitude of this increase is of the order of precision of the results, namely  $\pm 0.007$  per cent. if the three lots are treated as one population in the statistical sense. The results, in general, show that sodium carbonate obtained by heating sodium sesquicarbonate to 270° C is consistently of high purity.<sup>18,19</sup>

Samples of sodium sesquicarbonate representing the material from Series 3 were submitted to three independent laboratories for examination. The detailed methods employed were the same in each instance. The results returned by each of the laboratories are given in Table VII.

TABLE VII

PURITY OF WORKING-STANDARD SODIUM CARBONATE DETERMINED BY THREE INDEPENDENT LABORATORIES: EVALUATION WITH ULTIMATE STANDARD SILVER

Expt. No.	Purity of sodium carbonate from sodium sesquicarbonate, %	Evaluation by laboratory
1	100.03	A
2	99.96	B
3	99.95	B
4	99.98	B
5	100.03	C
6	100.03	C
Mean = 100.00		

These results confirm the values in Table VI.

ULTIMATE STANDARD SILVER

The pure silver prepared by electrolytic deposition from chemically pure silver has a high degree of purity, probably 99.995 per cent.

It was assumed to have a purity of 100.00 per cent. in the evaluation of the various lots of sodium sesquicarbonate.

Four methods were used to check the purity, namely—

- (a) direct gravimetric comparison with chemically pure silver of guaranteed minimum purity of 99.99 per cent. of silver, through *N* hydrochloric acid; the purity of ultimate standard silver was deduced to be 0.01 per cent. higher than that of the silver from which it was prepared,
- (b) chemical examination for impurities before and after purification; this showed that the original silver contained 0.0007 per cent. of copper and some carbon, but these two impurities could not be detected in the purified silver,
- (c) determination of the equivalent of working-standard iodine used for oxidimetry, which gave a value of 126.93 compared with the International Atomic Weight of 126.92, and
- (d) recent spectrographic examination, which gave the total impurities as not more than 0.002 per cent.



The thermal balance was lent by the courtesy of Messrs. Stanton Instruments Limited.

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## The Determination of Rubidium and Caesium in Rocks, Minerals and Meteorites by Neutron-activation Analysis

BY M. J. CABELL AND A. A. SMALES

A method is described for the determination of rubidium and caesium in rocks, minerals and meteorites by neutron-activation analysis. Except that simple precautions must be taken to eliminate the possibility of self-shielding of samples and standards during neutron irradiation, the results are not subject to interference by other constituents of the sample.

Each determination requires 15 to 300 mg of sample. After irradiation radiochemical separations with carriers present are based on ferric hydroxide scavengers, cobaltinitrite precipitations and cation-exchange chromatography. The purified rubidium and caesium fractions are finally recovered for counting as their chloroplatinates.

The samples examined have varied from 3.4 per cent. to  $4 \times 10^{-6}$  per cent. in rubidium content and from 7.5 per cent. to  $1 \times 10^{-6}$  per cent. in caesium content. They include an international inter-comparison suite of lepidolites, the two international standard rocks W1 and G1, samples from the Skaergaard intrusion of East Greenland and several meteorites.

Except at the lower end duplicate or triplicate determinations of rubidium contents usually agree within 5 per cent. and often within 2 per cent. Agreement between the results for caesium is rather less good. When it has been possible to compare results with those obtained by other methods, agreement has been excellent.

UNTIL quite recently accurate determinations of the concentrations of the alkali metals rubidium and caesium in many geological samples, especially when these concentrations are very small, have not been possible, because of the lack of suitable analytical methods. This limitation is particularly regrettable with rubidium, since the reliability of the rubidium-strontium method of geological-age determination depends upon determining rubidium and strontium with the highest possible accuracy.

In general, two methods have been employed for determining small amounts of the elements. The first, emission-spectrum analysis, which has been used by Ahrens<sup>1,2</sup> and others, suffers from the disadvantage that it depends on accurately known standards of composition very similar to the sample being available. The second, isotope-dilution analysis with enriched isotopes and the mass spectrometer, is undoubtedly superior from the points of view of both sensitivity and accuracy—a coefficient of variation of the results of 1 to 2 per cent. is attainable. It has been applied recently to rubidium determinations by Davis and Aldrich,<sup>3</sup> Tomlinson and Das Gupta,<sup>4</sup> Herzog and Pinson,<sup>5</sup> Pinson, Herzog, Backus and Cormier,<sup>6</sup> Schumacher,<sup>7</sup> Wetherill, Tilton, Davis and Aldrich<sup>8</sup> and by Webster and Smales.<sup>9</sup> Its application to the determination of caesium is complicated, but by no means eliminated, by the necessity for using a radioactive caesium isotope, since naturally occurring caesium is monoisotopic. So far, however, no geochemical applications for caesium determinations have been reported.

Neutron-activation analysis is another technique that is applicable to the determination of traces of rubidium and caesium. It has been used for their determination in sea-water, coal and sea-weed by Smales and Salmon,<sup>10</sup> and Cabell and Thomas<sup>11</sup> have used it for their determination in sodium-potassium liquid-metal alloys, but no general application in geochemistry has been reported so far. The advantages of the method, however, great sensitivity, specificity and freedom from contamination troubles, make it very suitable for the determination of traces of a large number of elements, and it has been chosen for this work.

An outline of the application of the technique to geological specimens has been given by Vincent and Smales<sup>12</sup> and need not be expanded further.

#### FEASIBILITY OF THE NEUTRON-ACTIVATION METHOD—

The nuclear characteristics of the isotopes involved when rubidium and caesium are subjected to neutron bombardment are given in Table I.

TABLE I  
NUCLEAR DATA FOR RUBIDIUM AND CAESIUM

Target nuclide	Abundance of nuclide in natural element, %	Isotopic activation cross-section, barns	Product of neutron irradiation	Radiation and energy of product nuclide, MeV	Half-life of product nuclide
<sup>85</sup> Rb	72.2	0.85	<sup>86</sup> Rb	$\beta^-$ 1.8 $\gamma$ 1.1	19.5 days
<sup>87</sup> Rb	27.8	0.14	<sup>88</sup> Rb	$\beta^-$ 5 $\gamma$ 3	18 minutes
<sup>133</sup> Cs	100.0	3 26	<sup>134m</sup> Cs <sup>134</sup> Cs	$e^-$ 0.13 $\beta^-$ 0.66 $\gamma$ 0.60, 0.79	3.1 hours 2.3 years

For practical purposes the short half-lives of <sup>86</sup>Rb and the metastable state of <sup>134</sup>Cs make them unsuitable for use when fairly lengthy chemical procedures are necessary to ensure radiochemical purity of the product. But <sup>88</sup>Rb and 2.3-year <sup>134</sup>Cs are quite suitable under these conditions and have been used exclusively in this work. It can be calculated that, by using these two radioactive nuclides and an irradiation time of 4 weeks in a flux of  $10^{12}$  thermal neutrons per sq. cm per second, *i.e.*, that of the Harwell Pile, the limit of detection under normal counting conditions is about  $6 \times 10^{-10}$  g for both caesium and rubidium.

#### EXPERIMENTAL

##### SAMPLING, STANDARDS AND IRRADIATION—

The samples for analysis were ground to less than 200-mesh B.S. sieve whenever possible. It proved difficult to grind lepidolite samples as fine as this, but small thin flakes proved to be quite suitable. Suitable quantities (10 to 250 mg) were weighed into small dry silica ampoules, which had been manufactured from silica tubing having an internal diameter of 4 or 6 mm, as described by Smales and Loveridge,<sup>13</sup> and the ampoules were immediately sealed. Weighed quantities (100 to 200 mg) of standard solutions were treated similarly, and samples and standards were packed side by side and irradiated in the "self-serve" positions of the Harwell Pile (see Cabell<sup>14</sup>) for periods of up to 4 weeks, or in the "rabbit" position for short periods.

Preliminary investigations showed that it was necessary to use solutions as standards. The chlorides are the only commercially available salts of caesium and rubidium that are sufficiently pure and thermally stable to serve as solid standards for the elements, but the chlorine nucleus has an average absorption cross-section of 32 barns, which is large enough for the solid chlorides to exhibit the phenomenon of self-shielding, *i.e.*, reduction of the effective neutron flux progressively through them, so that there is unequal irradiation of standard and sample. Of even greater importance with caesium is the fact that the caesium nucleus has several large neutron resonance absorption peaks, including one with a maximum of 2500 barns for neutrons of 6 eV, which is at least partly within the spectrum of the neutrons used for irradiations. The effect of this self-shielding is shown in Table II, in which the specific activity of different weights of solid caesium chloride is compared with that of a solution that was irradiated under identical conditions and for the same time. The bottom of the phials used in irradiations is conical rather than flat and it can be seen that the specific activity of the solid decreases as the phials are filled up until it reaches a constant value when the addition of more solid merely increases the height of solid in the phial without affecting the average diameter of the solid presented to the neutron beam.

TABLE II

## EFFECT OF SELF-SHIELDING ON THE SPECIFIC ACTIVITY OF CAESIUM CHLORIDE

Physical state of sample	Weight of caesium chloride in sample, mg	Concentration of solution, mg per g	Specific activity of caesium, counts per minute per mg
Liquid	0.153	1.000	34,870
Solid	5.3	—	27,000
Solid	14.5	—	26,800
Solid	24.4	—	24,700
Solid	42.9	—	24,900
Solid	45.9	—	24,800

By contrast, Table III shows that when the caesium chloride has been diluted one-hundredfold with water, further dilution, even another hundredfold, does not produce any significant increase in specific activity. Rubidium chloride in the solid state and in solution exhibits the same phenomena, but to a less marked extent.

TABLE III

## EFFECT OF DILUTION ON THE SPECIFIC ACTIVITY OF CAESIUM CHLORIDE SOLUTIONS

Concentration of caesium chloride solution, mg per g	Specific activity of caesium, counts per minute per mg
0.09994	35,500
0.3998	35,000
0.9994	35,600
0.9994	35,700
3.976	34,800
10.17	35,100

Average 35,300

Coefficient of variation 1.0 per cent.

The same two solutions were used as standards throughout this work. Specpure caesium and rubidium chlorides were dried to constant weight in platinum dishes at 170° C and a solution of each containing approximately 10 mg per g was made up accurately.

The rubidium content of the caesium chloride and the caesium content of the rubidium chloride were determined by neutron activation of the standard solutions. Two determinations of each showed that there were 45  $\mu$ g of rubidium per g of caesium chloride and 35  $\mu$ g of caesium per g of rubidium chloride. As rubidium and caesium attain approximately the same specific activity during irradiations of 1 day to 4 weeks, it was not necessary in the determinations either to separate the rubidium contained in the caesium chloride standards (or *vice versa*) or apply a correction for it, as its concentration was far too low to affect the result.

## DISSOLUTION AND SEPARATION OF THE ALKALI METALS—

After irradiation it is necessary to get the sample into solution with the carrier and in the same chemical form. The sodium peroxide sinter method of Seelye and Rafter<sup>15</sup> was used for this, but heating for a longer time and at a slightly lower temperature than those authors used was found necessary to obtain a good sinter and complete dissolution of beryls and lepidolites. Carriers were added to the samples directly after opening the irradiation tubes and before sintering. No special step was necessary to ensure chemical equilibrium between carrier and tracer, since the alkali metals can only exist as univalent cations in aqueous solutions.

The rubidium and caesium were separated from the other elements in the sample and from each other in two stages. In the first stage the alkali metals were collected together and freed from other constituents of the sample that had been made radioactive, and most of the sodium, by ferric hydroxide scavenges of the solution and precipitation of the alkali-metal cobaltinitrites. In the second stage the rubidium and caesium were separated from each other, and from potassium and residual amounts of the other alkali metals, by cation-exchange chromatography.

The separation of the alkali metals by cation-exchange chromatography has been demonstrated before, notably by Kayas,<sup>16</sup> but a more rapid procedure than any of those that have been published so far was required. The resin chosen was Zeo-Karb 315, which was known to be particularly favourable for alkali-metal separations. Two separate batches of the resin were used.

For the preparation of batch B sufficient "Normal" grade Zeo-Karb 315 was taken to form a column 1 metre long and 3.8 cm in diameter, and this was washed over a period of 2 days with 24 litres of 3 M hydrochloric acid to convert it to the hydrogen form and then with 5 litres of water. The resin was dried by exposure to the air, ground in a coffee grinder and sieved. The fraction passing through a sieve of aperture 0.179 mm and caught on a sieve of aperture 0.125 mm was collected and freed from "fines" by repeated decantation with water. Excess of water was poured off and the resin was washed twice with industrial methylated spirit and then with ether. Finally it was dried in a current of air and stored in a tightly stoppered bottle.

Batch A was treated in a similar manner, but was ground in a porcelain ball-mill. This method of grinding takes longer and possesses no advantage for this application over the use of a coffee grinder.

Although batches A and B were nominally of the same material, they had in fact been supplied by the makers at different times, and investigation showed that they possessed different properties. Weighed portions were dried to constant weight *in vacuo* at 80° C and were found to contain different proportions of water, but, even allowing for this, potentiometric titration in an atmosphere of nitrogen showed that their capacities were appreciably different. Hence 1 g of vacuum-dried resin from batch A required 2.25 milli-equivalents of sodium hydroxide for titration to pH 7.0, whereas 1 g of batch B required 2.51 milli-equivalents. Their swelling properties on addition of water were also different. Likewise their behaviour in ion-exchange chromatography differed and, although equal quantities from the same batch behaved reproducibly, the same quantity from the other batch required different volumes of eluent for a complete separation.

The separation of the alkali metals was studied by using synthetic mixtures of radioactive sodium, potassium, rubidium and caesium chlorides in proportions that approximated to those arising at the ion-exchange stage from genuine sample solutions. They were pre-treated as if they were genuine sample solutions and their elution from an ion-exchange column under different conditions was studied by monitoring the eluate for gamma radiation. It was found that sodium was completely removed by the pre-treatment and that the separation could be effected in one working day if 0.1 M hydrochloric acid was used to elute the potassium, and then 0.5 M hydrochloric acid for the rubidium fraction and 1.0 M hydrochloric acid for the caesium fraction.

Fig. 1 shows the successive elution of the alkali metals from a column made by packing 25.0 g of resin A in a tube of approximately 1 cm diameter. Fig. 2 shows a similar separation on a column made from 21.6 g of resin B in a tube of the same diameter—this occupied almost exactly the same volume as 25.0 g of resin A. Based on experiments such as these, it was possible to set conditions under which the alkali metals of sample solutions could be separated

into pure fractions, even though the separation could not be followed by monitoring the eluate as described above, since the radioactivity of sample solutions is too small for this to be practicable. The actual conditions arrived at are set out in Table IV.

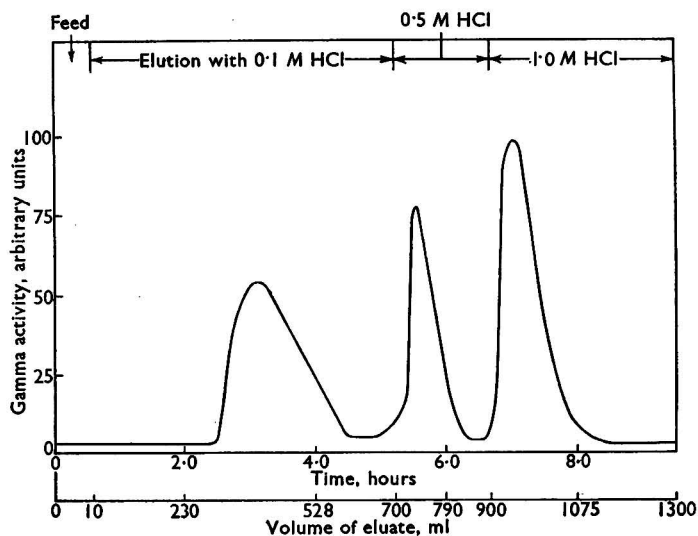


Fig. 1. Separation of potassium, rubidium and caesium by cation-exchange chromatography in a column containing 25.0 of Zeo-Karb 315 (-85 to +120 B.S. sieve, batch A)

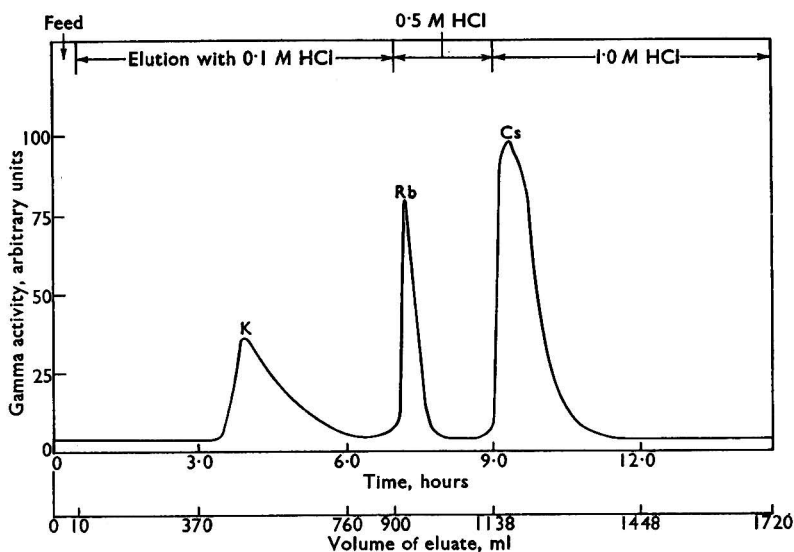


Fig. 2. Separation of potassium, rubidium and caesium by cation-exchange chromatography in a column containing 21.6 g of Zeo-Karb 315 (-85 to +120 B.S. sieve, batch B)

#### DETERMINATION OF CHEMICAL YIELD—

Recovery of the alkali metal from each acidic fraction of eluate was achieved by evaporating the solution to dryness, dissolving the residue in water, adding sufficient sodium hydroxide to make the extract alkaline, filtering, neutralising with acetic acid and precipitating the alkali-metal cobaltinitrite. Duval<sup>17</sup> has shown, however, that rubidium and caesium

cobaltinitrites are unsuitable for the gravimetric determination of the elements, whereas the chloroplatinates are easily obtained as stoichiometric compounds. The cobaltinitrites were therefore dissolved in nitric acid, and ethanol and then a solution of hexachloroplatinic acid were added. The precipitate was washed with ethanol, transferred to a weighed counting tray, dried under an infra-red lamp and weighed.

TABLE IV  
CONDITIONS USED FOR THE SEPARATION OF THE ALKALI METALS ON  
COLUMNS OF ZEO-KARB 315

	Resin A	Resin B
Weight of resin taken, g .. .. .	25.0	21.6
Feed solution, ml .. .. .	5, plus a 5-ml wash with water	5, plus a 5-ml wash with water
Flow rate for applying feed, ml per hour .. .. .	30	30
Flow rate used throughout elution, ml per hour .. .. .	<150	<150
Volume of rejected potassium fraction, ml of 0.1 M hydrochloric acid	700	900
Volume of pure rubidium fraction, ml of 0.5 M hydrochloric acid ..	100	100
Volume of rejected mixed rubidium and caesium fraction, ml of 0.5 M hydrochloric acid .. .. .	100	120
Volume of pure caesium fraction, ml of 1.0 M hydrochloric acid ..	150	200

This procedure has other advantages. First, any sodium from the added sodium hydroxide that had been co-precipitated with the cobaltinitrite is dissolved in the ethanol and removed under these conditions and, secondly, the alkali-metal chloroplatinates are dried more easily. Whereas Duval<sup>17</sup> has shown that caesium hexachloroplatinate that has been precipitated from aqueous solution does not lose all its water until heated to 200° C, we found that precipitation from ethanolic solution and washing with ethanol gave a product that was stoichiometric and anhydrous on being heated to 80° C and did not lose weight thereafter, at least up to 370° C.

Rubidium and caesium chloroplatinates are easily slurried evenly into aluminium counting trays and form compact adhering cakes that are most suitable for counting. The chemical yields obtained in practice varied between 50 and 70 per cent. for samples and between 80 and 90 per cent. for standards.

#### MEASUREMENT OF RADIOACTIVITY—

The alkali-metal chloroplatinates were counted by using an EHM2 thin-window Geiger tube and a conventional Geiger beta - gamma-counting assembly. At least 10<sup>4</sup> counts were recorded whenever practicable. The sources used were 5 sq. cm in area and it was shown that no self-absorption or back-scattering correction was necessary for rubidium chloroplatinate sources that were less than 10 mg per sq. cm in thickness; greater thicknesses could probably be tolerated without a correction being necessary, but these were never used. No self-absorption or back-scattering corrections were necessary with caesium chloroplatinate sources either, provided that their thickness was within the range 4 to 10 mg per sq. cm, as it always was in practice. The combined effects of self-absorption and back-scattering on the counting-rate of caesium chloroplatinate are seen in Table V. The apparent specific activity, as measured by Geiger counting, of sources of varying thicknesses prepared from a common stock is recorded. The difference in apparent specific activity between sources of thickness 4.4 mg per sq. cm and those of thickness 9.7 mg per sq. cm is less than 3 per cent. Sources from samples and standards used in analyses seldom differed by as much as 2 mg per sq. cm in thickness, so the error due to these factors in using the two counting rates as a direct measure of their alkali-metal contents would nearly always be less than 1 per cent., *i.e.*, less than the statistical error involved in counting either of them.

TABLE V  
COMBINED EFFECTS OF SELF-ABSORPTION AND BACK-SCATTERING ON CAESIUM  
CHLOROPLATINATE SOURCES

Thickness of source, mg per sq. cm .. .. .	1.29	1.44	2.15	2.61	2.89	4.40	5.48	5.63	6.62	9.67
Specific activity of source, counts per minute per mg	74.5	75.6	77.4	78.1	78.6	80.6	79.8	79.3	78.3	78.4

Another correction that must be considered when rubidium chloroplatinate sources of very low beta - gamma activity are being counted is the radioactivity of the <sup>87</sup>Rb, which

comprises 27.8 per cent. of the naturally occurring rubidium used as the carrier for the traces of radioactive rubidium in the sample. A source of known weight of rubidium chloroplatinate prepared from natural rubidium was kept for this purpose and this was counted directly after samples for which a correction was thought to be necessary. With this source placed within 1 mm of the Geiger tube, the count recorded was only 2.2 counts per minute per mg of rubidium. Under the most unfavourable counting conditions used in practice, *i.e.*, with the sources within 1 cm of the Geiger tube, the correction never amounted to as much as double the counter background correction; usually it was quite insignificant.

#### CONFIRMATION OF RADIOCHEMICAL PURITY—

The preliminary experiments on the separation of the alkali metals by ion exchange showed that pure alkali-metal fractions could be obtained without difficulty. In applying the information obtained from these experiments to the sample solutions, large safety factors were allowed in deciding which fractions of the eluate to accept and which to reject, so that any small variations in column behaviour would be allowed for and not affect the purity of the product. Nevertheless an essential part of the neutron-activation method is the confirmation of the radiochemical purity of the products.

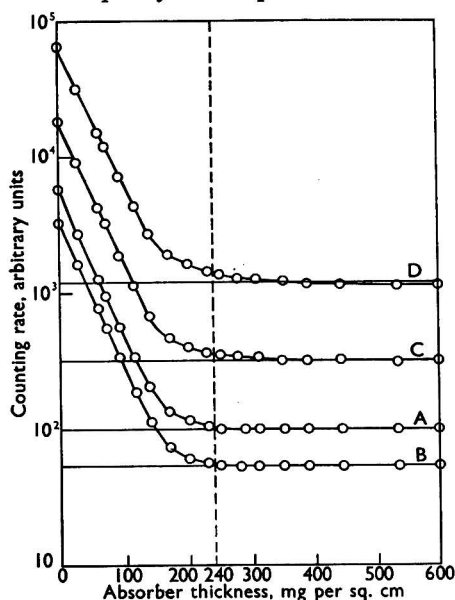


Fig. 3. Absorption curves for caesium: curve A, pure caesium standard; curve B, caesium separated from a sample; curve C, caesium and added rubidium (ratio of beta activity of rubidium to beta activity of caesium is 0.005); curve D, caesium and added rubidium (ratio of beta activity of rubidium to beta activity of caesium is 0.014)

Decay curves are possible for rubidium and have been used by Smales and Salmon,<sup>10</sup> but ideally they require four half-lives, *i.e.*, 80 days, for certainty of radiochemical purity. They are not, of course, practicable for caesium.

Beta-absorption curves are suitable for the confirmation of caesium purity and have been used in this work. Typical examples are displayed in Fig. 3 and show clearly that the beta particles of maximum energy produced by caesium just fail to penetrate an absorber having a thickness of 240 mg of aluminium per sq. cm as expected for a beta particle of energy 0.66 MeV. The Figure also shows the curves produced when small amounts of rubidium activity are deliberately added to pure caesium sources. It is clear that if rubidium impurity were present in caesium products it could be detected with considerable sensitivity in this way, but none has ever been found in practice.

Beta-absorption curves have also been used to confirm rubidium radiochemical purity. The most energetic beta particles produced by rubidium just fail to penetrate an absorber having a thickness 880 mg of aluminium per sq. cm and this is clearly shown in the examples displayed in Fig. 4, but the presence of caesium impurity in even quite large amounts could escape detection very easily, as is demonstrated by another curve in the Figure, which was obtained by deliberately adding radioactive caesium to a pure rubidium source. For this reason a close similarity of the beta-absorption curves obtained from sample and standard is not a very reliable test for rubidium radiochemical purity.

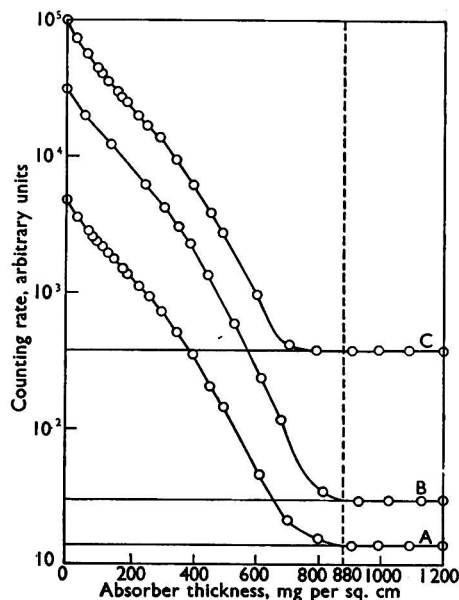


Fig. 4. Absorption curves for rubidium: curve A, pure rubidium standard; curve B, rubidium separated from a sample; curve C, rubidium and added caesium (ratio of beta activity of caesium to beta activity of rubidium is 0.15)

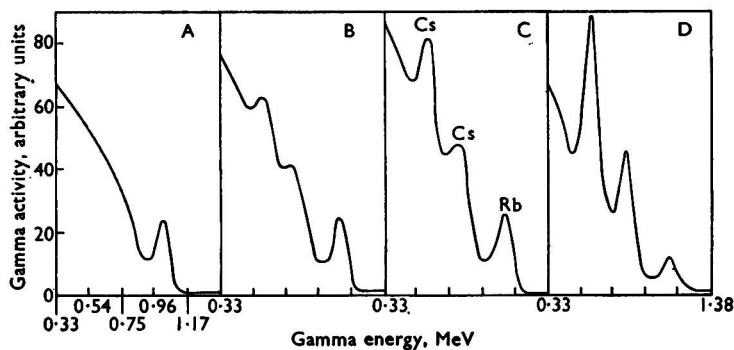


Fig. 5. Gamma-ray spectra for rubidium: curve A, pure rubidium standard; curve B, rubidium and added caesium (ratio of beta activity of caesium to beta activity of rubidium is 0.006); curve C, rubidium and added caesium (ratio of beta activity of caesium to beta activity of rubidium is 0.011); curve D, rubidium and added caesium (ratio of beta activity of caesium to beta activity of rubidium is 0.057)



In contrast to this, the presence of a small amount of caesium impurity in a rubidium source is readily shown by the gamma spectrum of the mixture. The reason for this is that for each beta particle produced by the disintegration of a  $^{134}\text{Cs}$  nucleus approximately two gamma photons are also produced, whereas the production of a beta particle by a disintegrating  $^{86}\text{Rb}$  nucleus is accompanied by the production of a gamma photon only once in about five times. Moreover, each gamma photon produced by a disintegrating  $^{134}\text{Cs}$  nucleus is of lower energy than a corresponding gamma photon from a  $^{86}\text{Rb}$  nucleus and is recorded with approximately twice the sensitivity by the gamma spectrometer (where the height of the gamma peak is taken as the criterion of sensitivity). These two effects reinforce one another so that when sources of  $^{134}\text{Cs}$  and  $^{86}\text{Rb}$  of equal beta activity are examined in the gamma spectrometer the caesium source produces a gamma peak many times the height of that given by the rubidium source.

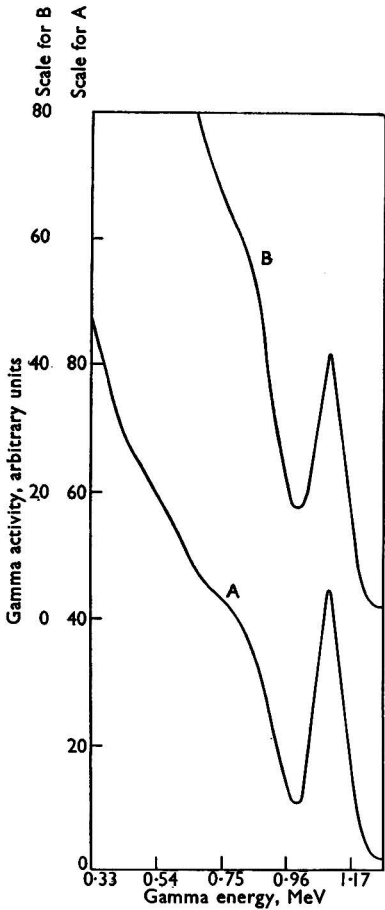


Fig. 6. Gamma-ray spectra for rubidium: curve A, rubidium sample separated from a lepidolite; curve B, pure rubidium standard

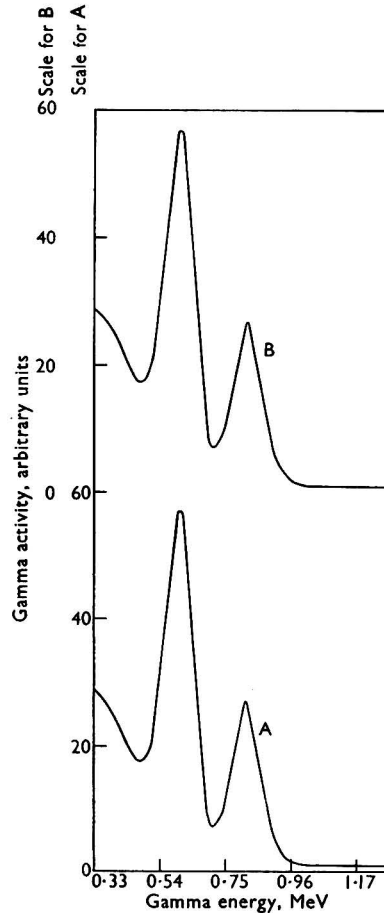


Fig. 7. Gamma-ray spectra for caesium: curve A, caesium sample separated from a lepidolite; curve B, pure caesium standard

This is seen in Fig. 5, where the gamma spectrum obtained from a pure rubidium source is compared with those obtained from similar rubidium sources to which caesium impurity has been added in known amounts. It can be seen that, when the beta activity of the caesium is only 0.6 per cent. of the rubidium beta activity (both being measured by a Geiger counter before mixing), the gamma spectrum still shows this small amount very clearly. Fig. 6 shows the gamma spectra obtained from some rubidium separated from an irradiated lepidolite

and that due to a standard rubidium source; no evidence of caesium impurity can be detected. For comparison purposes the gamma spectra of a pure caesium source and a caesium sample separated from a lepidolite are displayed in Fig. 7.

#### METHOD

##### PROCEDURE—

Grind the sample for analysis to less than 200-mesh B.S. sieve or as finely as practicable. Weigh a suitable quantity (10 to 250 mg) into a dry silica ampoule and, if necessary (see later), add a diluent, seal the tube and mix the contents thoroughly. Prepare some clean dry transfer pipettes and rub the tips with a small piece of cotton-wool that has been dipped in a dilute solution of dimethyldichlorosilane in carbon tetrachloride. Wipe the tips clean and use the pipettes to transfer 100 to 200-mg amounts of standard solutions of Specpure rubidium and caesium chloride of accurately known concentration (less than 1 per cent.) to weighed ampoules. Weigh again and seal. Mark the ampoules for identification, pack the samples together with duplicate standards for each alkali metal, and irradiate them in the Harwell Pile for suitable periods of up to 4 weeks. After irradiation allow the ampoules to "cool" sufficiently before handling.

Weigh accurately approximately 40 mg of Specpure caesium chloride and 40 mg of Specpure rubidium chloride into a platinum crucible and cover with a thin layer of AnalaR sodium peroxide. Take a sample ampoule, tap it until the contents fall to the bottom, scratch the constriction with a diamond and open the ampoule. Invert the tube and tap it until the contents fall into the crucible and then add more sodium peroxide and mix the contents of the crucible thoroughly with a piece of flattened platinum wire. Cover with a thin layer of sodium peroxide (of which the total amount used need not exceed 4 to 5 g).

Heat the crucible in the furnace for 1 hour at, but not exceeding, 470° C. Cool the crucible by dipping the outside in water, invert it and tap the bottom so that the sinter falls into a 250-ml conical beaker. Cover with a watch-glass and allow to cool. Fill the crucible with water to dissolve any of the sinter remaining and pour the solution into the beaker. Repeat until the sinter is covered with water. Boil until the sinter is dissolved and no more bubbles are evolved. Cool, add 2 ml of a solution of ferric chloride in hydrochloric acid (10 mg of iron per ml), mix and cool again. Now rapidly add 10-ml amounts of concentrated hydrochloric acid at a time, swirling the contents and cooling the beaker after each addition, until a clear yellow solution is obtained.

Spin the ampoules containing the standard solutions in a centrifuge until the liquid is collected at the bottom of each tube. Open them in the same way as the samples, but observe caution. Considerable pressure is released as the ampoules are broken, although this does not result in any loss. Without loss of time transfer the contents to a 100-ml calibrated flask with a transfer pipette and with the same pipette thoroughly wash both parts of the ampoule with dilute hydrochloric acid, transferring the washings to the flask. Add two drops of concentrated hydrochloric acid and make up to the mark. Take suitable aliquots for direct use or dilution.

##### PREPARATION OF THE SAMPLE FOR THE COLUMN—

Treat the sample solution in portions of about 40 ml in separate centrifuge tubes. To each add 5 drops of phenolphthalein and then 6 M sodium hydroxide dropwise until the solution is just alkaline. Spin in a centrifuge and filter. Acidify the filtrate with glacial acetic acid, add 1 ml of ferric chloride solution (10 mg of iron per ml) and again make alkaline with 6 M sodium hydroxide. Spin in a centrifuge and filter.

Acidify the filtrate with acetic acid, add 10 ml of a freshly prepared 10 per cent. solution of sodium cobaltinitrite, stir and set aside for at least 5 minutes in an ice bath. Spin in a centrifuge and wash three times with water.

Collect all the cobaltinitrite precipitates from the same sample together, remove any supernatant liquid and add 2 ml of diluted nitric acid (1 + 1). Heat with shaking over a bunsen flame until the precipitate has dissolved. Transfer the solution to a small beaker and remove all the water and acid by evaporation under an infra-red lamp until a blue tarry residue is left. Dissolve in 5 ml of water and filter if the solution is not clear. The solution is now ready for feeding to the column.

## THE ION-EXCHANGE SEPARATION—

It has been emphasised already that each batch of resin must be treated on its merits. Prepare a batch of Zeo-Karb 315 (if this is not available a resin with similar cation-exchange properties may be used) of particle size such that it passes through a No. 85 B.S. sieve and is caught on a No. 120 B.S. sieve. Determine the weight of resin required such that its volume is approximately 36 ml when prepared for use, and transfer this amount to a glass tube 1 cm in diameter that has been shaped to form a column of a conventional kind.

Dissolve 40 mg of rubidium chloride, 40 mg of caesium chloride, 190 mg of potassium chloride and 60 mg of cobalt as chloride in 5 ml of water and feed this solution to the column at a flow-rate not exceeding 0.5 ml per minute. Allow the liquid level to fall to the top of the column and then add 5 ml of washings, and again allow the level to sink to the top of the column. Using a reservoir of 0.1 *M* hydrochloric acid supported above the column and feeding it by a siphon flow, elute at a flow-rate as near to, but not exceeding, 2.5 ml per minute as possible. A total pressure of about 170 cm of liquid above the bottom of the column will be required. Determine the change in concentration of potassium in the eluate by a suitable method and continue elution until all the potassium has been removed. Now elute with 0.5 *M* hydrochloric acid at a flow-rate not exceeding 2.5 ml per minute and determine the rubidium elution curve. Finally use 1.0 *M* hydrochloric acid to recover the caesium.

From the results obtained in this way devise a scheme for obtaining pure rubidium and caesium fractions from the sample solutions, making allowance for the rejection of cross-contaminated fractions. Prepare similar columns for these separations. After each caesium fraction has been recovered regenerate the column for the next sample solution by passing 1500 ml of 3 *M* hydrochloric acid through it over a period of 8 hours, followed by water until the pH of the eluate is 4.0 or greater.

## FINAL PURIFICATION AND RECOVERY—

Treat both the rubidium and the caesium fractions as follows. Evaporate to dryness on the hot-plate and dissolve the residue in 20 ml of hot water. Transfer to a centrifuge tube and cool. Add 2 drops of phenolphthalein, make alkaline with 6 *M* sodium hydroxide, spin in a centrifuge and filter (the caesium fraction will contain cobaltic hydroxide). Make the filtrate acid with acetic acid and add 10 ml of a freshly prepared 10 per cent. solution of sodium cobaltinitrite. Set the solution aside for at least 5 minutes in an ice bath while the precipitate forms, then spin in a centrifuge and wash the precipitate three times with distilled water. Add 2 ml of diluted nitric acid (1 + 1) and heat over a bunsen flame until the precipitate has dissolved. Cool. Add another 2 ml of diluted nitric acid and then 15 ml of anhydrous industrial methylated spirit and 1 ml of a 10 per cent. solution of hexachloroplatinic acid. Stir and set the solution in an ice bath for 10 minutes while the precipitate forms, then spin in a centrifuge and wash the precipitate three times with 74 O.P. industrial methylated spirit. Make a slurry of the precipitate with a few drops of industrial methylated spirit and transfer it to a weighed aluminium tray, dry under an infra-red lamp, cool and re-weigh in order to determine the chemical yield.

## STANDARDS—

Add carriers to the standards and treat them in exactly the same way as the sample solutions throughout. If, however, they have been analysed and it is known that the rubidium chloride does not contain more than traces of caesium and *vice versa*, the ion-exchange step and the second cobaltinitrite precipitation may be omitted. Arrange that the standards and samples for counting are of approximately the same weight and between 5 and 10 mg per sq. cm in thickness.

## COUNTING—

Count the precipitate of caesium chloroplatinate or rubidium chloroplatinate for beta-gamma activity, using an end-window Geiger tube of the GM4 or EHM2 type, and count the standards directly afterwards under identical conditions. Obtain a total count of at least  $10^4$  counts whenever practicable and make use of lower geometry and absorbers so that the counting rate does not exceed 5000 counts per minute. Correct the measured activities for background, counter dead-time and, with rubidium, the natural activity of the rubidium carrier.

Calculate the amount of alkali metal in the sample  $x$ , by means of the relationship—

$$\frac{\text{Mass of } x \text{ in sample}}{\text{Mass of } x \text{ in standard}} = \frac{\text{Activity of } x \text{ from sample corrected for 100 per cent. recovery}}{\text{Activity of } x \text{ from standard corrected for 100 per cent. recovery}}$$

using the conversion factors—

$$\begin{aligned} 10 \text{ mg of Rb} &\equiv 14.14 \text{ mg of RbCl} \\ 10 \text{ mg of Cs} &\equiv 12.68 \text{ mg of CsCl} \\ 10 \text{ mg of Rb} &\equiv 33.86 \text{ mg of Rb}_2\text{PtCl}_6 \\ 10 \text{ mg of Cs} &\equiv 25.35 \text{ mg of Cs}_2\text{PtCl}_6 \end{aligned}$$

Note that when the sample or standard contains a weight of alkali metal significant in comparison with that used for the carrier this must be taken into account when calculating the chemical yields.

Finally confirm the radiochemical purity of the products by means of half-life determination, beta-absorption curves and gamma-spectra determinations as appropriate.

## RESULTS

### MINERALS—

Table VI records the results obtained for the alkali-metal contents of an International Intercomparison Suite of Lepidolites that had been prepared at the Massachusetts Institute of Technology and supplied by Dr. L. H. Ahrens, Department of Geology and Mineralogy, University of Oxford. For comparison purposes the rubidium figures obtained by two groups of workers by isotope-dilution analysis are also recorded. The results for two other lepidolites that were collected by Prof. H. Bassett in Tanganyika are also given.

TABLE VI

RUBIDIUM AND CAESIUM CONTENTS OF AN INTERNATIONAL SUITE OF LEPIDOLITES, TWO OTHER LEPIDOLITES AND PRECIPITATED SILICA

Sample and origin	Sample weight, mg	Rubidium found, %	Caesium found, %	Average rubidium found, %	Average caesium found, %	Rubidium found by Pinson <i>et al.</i> , <sup>18</sup> %	Rubidium found by Aldrich <i>et al.</i> , <sup>19</sup> %
<i>International intercomparison suite—</i>							
L-N45, Bikita Quarry, S. Rhodesia	24.95 24.84	3.40 3.42	0.290 0.302	3.41	0.296	3.29	3.31
L-A106, Bob Ingersoll Mine, S. Dakota	21.89 28.40 29.44 28.48	1.21 1.29 1.34 —	0.146 0.137 0.139 0.154	1.28	0.144	1.26	1.21 1.23 1.16
L-A107, Pala Mine, S. California	15.20 23.47	1.74 1.77	0.248 0.259	1.76	0.253	1.39	1.76
L-A109, along Winnepeg River, S.E. Manitoba	19.54 20.97 26.70 23.36	2.23 2.24 2.26 —	0.170 0.164 0.163 0.176	2.24	0.168	2.08	2.20
L-A110 (b), Varutrask, Sweden	20.81 21.62	1.58 1.62	0.173 0.179	1.60	0.176	1.85	2.05
<i>Other lepidolites—</i>							
B1, Hombola, Tanganyika, collected 9/11/51	20.59 14.22	1.15 1.16	0.293 0.288	1.16	0.290	—	—
B2, Zati, near Hombola, Tanganyika, collected 24/7/52	22.87 18.63	2.35 2.38	0.831 0.839	2.37	0.835	—	—
<i>Silica—</i>							
Specpure precipitated silica, No. 8141	296.6 321.6 297.0	$7 \times 10^{-7}$ $5 \times 10^{-7}$ $4 \times 10^{-7}$	$6 \times 10^{-6}$ $5 \times 10^{-6}$ $6 \times 10^{-6}$	$5 \times 10^{-7}$	$6 \times 10^{-6}$	—	—

With minerals such as lepidolites it was thought necessary to take precautions against self-shielding in the samples. Lepidolites may contain up to 5 per cent. by weight of lithium

and, since the absorption cross-section of the  ${}^6\text{Li}$  nucleus is 950 barns and  ${}^6\text{Li}$  constitutes 7.5 per cent. of natural lithium, this concentration is sufficient to increase the mean absorption cross-section for each atom in a lepidolite by a factor fifty to two hundred times that of an atom in an igneous rock. The samples that are given in Tables VI and VII were therefore diluted (after weighing) at least ten times by weight (and many more times by volume, which is the important thing) with Specpure precipitated silica. The silica was analysed separately by neutron-activation analysis with the results also given in Table VI. Its content of caesium and rubidium was too low to make a correction of the results for the minerals necessary.

Table VII records the results obtained for a series of minerals supplied by Dr. J. M. Axelrod of the United States Department of the Interior, Geological Survey. Dr. Axelrod has analysed the same samples by X-ray spectroscopy and by flame photometry. His results are also recorded in Table VII for comparison. For X-ray spectroscopy he claims a sensitivity of 0.02 per cent. of rubidium oxide or 0.1 per cent. of caesium oxide and an accuracy of 10 per cent. of the amount present or the sensitivity, whichever is larger.

TABLE VII  
RUBIDIUM AND CAESIUM CONTENTS OF SOME MINERALS

Sample and origin	Sample weight, mg	Rubi- dium oxide found, %	Cae- sium oxide found, %	Rubidium oxide found by—			Caesium oxide found by—		
				neutron acti- va- tion (average), %	X-ray spectro- scopy,* %	flame photo- metry,* %	neutron acti- va- tion (average), %	X-ray spectro- scopy,* %	flame photo- metry,* %
143024, lepidolite, from Stewart's Mine, Pala, California	16.91	1.50	0.81	1.50	1.51	1.58	0.81	0.8	0.89
	23.05	1.49	0.81						
143025, lepidolite, from San Diego Mine, Mesa Grande	42.00	1.12	0.362	1.12	1.12	1.21	0.363	0.4	0.38
	18.94	1.12	0.364						
143029, lepidolite, from Foote Mineral Co., 51A-32-2	29.98	3.13	0.288	3.18	3.20	3.4	0.294	0.3	0.37
	20.35	3.23	0.299						
144206, lepidolite, from Stewart's Mine, Pala, California	22.58	1.44	0.082	1.45	1.47	1.40	0.083	0.1	0.06
	20.10	1.47	0.084						
143950, white beryl, from Le Grange, Georgia	17.62	0.0211	0.152	0.021	0.02	<0.01	0.150	0.1	0.12
	14.05	0.0214	0.149						
143952, morganite, from Madagascar	17.51	0.0202	7.52	0.020	0.02	<0.01	7.52	7.9	7.6
143006, microcline from Tourmaline Queen Mine, Pala, California	16.06	0.065	0.0084	0.065	—	0.10	0.0082	—	0.00
	19.25	0.065	0.0080						
143948, beryl, from Bumpus Quarry, Albany, Maine	29.72	0.0066	0.054	0.0066	0.01	<0.01	0.054	0.0	<0.05
	51.79	0.0066	0.055						

\* Figures supplied by Dr. J. M. Axelrod, U.S. Geological Survey.

#### ROCKS—

The results of analyses of the typical basic and acidic rocks W1 and G1, which have been suggested as international standards for the determination of both major and minor constituents of igneous rocks, are given in Table VIII. The rubidium results are compared with those of workers at A.E.R.E., Harwell (Webster and Smales<sup>9</sup>), and the Massachusetts Institute of Technology (Herzog and Pinson<sup>5</sup>) both of whom used isotope-dilution analysis. The new values for rubidium are the result of further work since the Note by Smales<sup>20</sup> and are preferred to those quoted there, which were, for G1, 221, 254 and 243 p.p.m. and, for W1, 27, 29 and 26 p.p.m.

TABLE VIII

RUBIDIUM AND CAESIUM CONTENTS OF THE INTERNATIONAL STANDARD ROCKS W1 and G1

Sample and origin	Sample weight, mg	Rubidium found, p.p.m.	Caesium found, p.p.m.	Rubidium found by—			Caesium found by neutron activation (average), p.p.m.
				neutron activation (average), p.p.m.	isotope-dilution method at A.E.R.E., p.p.m.	isotope-dilution method at M.I.T., p.p.m.	
G1, granite from Westerly, Rhode Island	199.7	217	1.51	219	214	216	1.5
	194.0	219	1.48				
	246.1	222	1.54				
W1, diabase from Center-ville, Virginia	200.5	20.6	1.03	21.3	21.3	28.5	1.08
	196.9	21.6	1.13				
	404.5	21.8	1.07				

A number of samples taken from various parts of the Skaergaard intrusion of East Greenland were also analysed. They were supplied by Prof. L. R. Wager and Dr. E. A. Vincent of the Department of Geology and Mineralogy, University of Oxford. The results are given in Table IX, but no comparison figures by other workers are available.

TABLE IX

RUBIDIUM AND CAESIUM CONTENTS OF SAMPLES FROM THE SKAERGAARD INTRUSION OF EAST GREENLAND

Sample and origin	Sample weight, mg	Rubidium content, p.p.m.	Caesium content, p.p.m.	Average rubidium content, p.p.m.	Average caesium content, p.p.m.
EG3058, transgressive granophyre sill ..	171.4	92	0.28	96	0.34
	170.5	97	0.40		
	196.2	98	0.35		
EG4489, transgressive granophyre sill ..	169.4	45.9	0.59	47.2	0.60
	161.0	47.5	0.61		
	205.9	48.1	—		
EG4332, hedenbergite granophyre ..	102.7	39.4	0.29	42	0.32
	101.3	44.5	0.34		
EG4330, fayalite ferrogabbro .. ..	105.9	21.4	0.18	21.9	0.19
	104.3	22.4	0.20		
EG4328, upper ferrogabbro .. ..	223.0	12.2	0.47	12.5	0.49
	221.7	12.6	0.51		
	201.2	12.6	0.50		
EG5181, lower ferrogabbro .. ..	103.4	2.3	<0.1	2.4	<0.1
	104.9	2.5	—		
EG4427, middle gabbro .. ..	104.8	1.0	<0.1	1.0	<0.1
	102.2	0.9	<0.1		
EG5086, hypersthene-olivine-gabbro ..	102.4	2.4	<0.1	2.5	<0.1
	104.0	2.5	<0.1		
EG1851, perpendicular feldspar rock ..	247.7	2.08	0.155	2.3	0.15
	192.9	2.33	0.159		
	172.1	2.36	0.143		
EG4526, gabbro picrite .. ..	180.7	5.3	—	5.6	0.36
	220.5	5.5	0.365		
	198.5	5.9	0.363		
EG4507, chilled marginal gabbro .. ..	101.3	5.8	0.09	5.8	0.10
	107.8	5.9	0.12		

## METEORITES—

Several stony meteorites have also been analysed for their rubidium and caesium contents. The sample of "Homestead" meteorite had had 10.7 per cent. by weight of metal extracted, but otherwise drillings (about 1 g) of whole meteorite were taken and mixed before sampling, without any attempt being made to separate the dispersed metallic phase. The results are given in Table X.

TABLE X  
RUBIDIUM AND CAESIUM CONTENTS OF SOME STONY METEORITES

Sample and origin	Sample weight, g	Rubidium content found, p.p.m.	Caesium content found, p.p.m.	Average rubidium content, p.p.m.	Average caesium content, p.p.m.																																																																																																
AMNH100,* from Forest City, Winnebago Co., Iowa	0.1701	3.01	0.101	3.04	0.098																																																																																																
	0.1611	3.06	0.096			AMNH1018, from Ness Co., Kansas . .	0.1175	2.88	0.036	2.90	0.039	0.1496	2.93	0.041	OUM2,† from Faha, Co. Limerick, Rep. Ireland	0.1903	2.19	0.099	2.28	0.099	0.1382	2.37	0.099	Homestead,‡ from Homestead, Iowa	0.1445	2.96	0.09	3.15	0.07	0.1555	3.00	0.06	0.1140	3.29	0.06	0.1032	3.34	—	AMNH2454, from Modoc, Scott Co., Kansas	0.2637	2.91	0.09	2.97	0.08	0.1877	2.98	0.08	0.1485	3.01	0.07	0.2439	—	0.07	AMNH2399, from Long Island, Phillips Co., Kansas	0.1140	2.05	0.02	2.11	0.01	0.1239	2.09	0.01	0.1174	2.15	0.01	0.2215	2.15	0.01	AMNH1043, from Bluff, Fayette Co., Texas	0.1165	1.00	0.01	1.01	0.01	0.1123	1.00	0.01	0.1306	1.03	—	0.1069	1.03	—	AMNH2497, from Johnstown, Weld Co., Colorado	0.1750	0.04	0.005	0.04	0.007	0.1564	0.04	0.007	0.3392	0.05	—	0.2281	0.05	0.008			
AMNH1018, from Ness Co., Kansas . .	0.1175	2.88	0.036	2.90	0.039																																																																																																
	0.1496	2.93	0.041			OUM2,† from Faha, Co. Limerick, Rep. Ireland	0.1903	2.19	0.099	2.28	0.099	0.1382	2.37	0.099	Homestead,‡ from Homestead, Iowa	0.1445	2.96	0.09	3.15	0.07	0.1555	3.00	0.06		0.1140	3.29	0.06			0.1032	3.34	—	AMNH2454, from Modoc, Scott Co., Kansas	0.2637	2.91	0.09	2.97	0.08		0.1877	2.98	0.08			0.1485	3.01	0.07	0.2439	—	0.07	AMNH2399, from Long Island, Phillips Co., Kansas	0.1140	2.05		0.02	2.11	0.01			0.1239	2.09	0.01	0.1174	2.15	0.01	0.2215	2.15	0.01		AMNH1043, from Bluff, Fayette Co., Texas	0.1165	1.00			0.01	1.01	0.01	0.1123	1.00	0.01	0.1306	1.03	—		0.1069	1.03	—			AMNH2497, from Johnstown, Weld Co., Colorado	0.1750	0.04	0.005	0.04	0.007	0.1564	0.04	0.007	0.3392	0.05	—
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Homestead,‡ from Homestead, Iowa	0.1445	2.96	0.09	3.15	0.07																																																																																																
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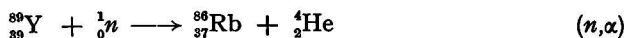
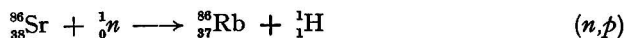
\* Kindly supplied by Dr. Brian H. Mason, American Museum of Natural History, New York, N.Y.

† Kindly supplied by Dr. L. H. Ahrens, Department of Geology and Mineralogy, University of Oxford.

‡ Kindly supplied by Drs. W. H. Pinson and L. F. Herzog, Department of Geology, Massachusetts Institute of Technology.

#### INTERFERING ELEMENTS

In neutron-activation analysis the possibility that radioactive nuclides of the elements being determined may arise by other nuclear processes than the one under consideration, must always be borne in mind. Of these ( $n,p$ ), ( $n,\alpha$ ) and ( $n,f$ ) reactions are the most likely. Hence, apart from the  $n,\gamma$  reaction with  $^{85}\text{Rb}$ ,  $^{86}\text{Rb}$  may be produced by any of the following reactions—



Reactions of a similar nature, which give rise to  $^{134}\text{Cs}$  and other radioactive caesium isotopes, are possible when barium, lanthanum and uranium are irradiated with neutrons. If therefore any of these elements, or strontium or yttrium, are present in samples and such reactions do take place to any appreciable extent, they will, of course, increase the apparent  $n,\gamma$  induced radioactivity due to alkali metals in the samples and lead to results that are too high.

To determine whether such interferences are appreciable, known weights of Specpure barium and strontium carbonates, and lanthanum, yttrium and uranium oxides, were irradiated, together with rubidium and caesium standards, and analysed for their "apparent" alkali-metal contents by the method described above. The results are given in Table XI.

TABLE XI

PSEUDO-RUBIDIUM AND PSEUDO-CAESIUM CONTENTS OF ELEMENTS THAT GIVE RISE TO RADIOACTIVE NUCLIDES OF RUBIDIUM AND CAESIUM ON NEUTRON BOMBARDMENT, BY REACTIONS OTHER THAN  $n,\gamma$

Element irradiated	"Apparent" rubidium content, p.p.m.	Average, p.p.m.	"Apparent" caesium content, p.p.m.	Average, p.p.m.
Strontium .. ..	0.71 } 0.69 }	0.70	<0.1	—
Yttrium .. ..	0.18 } 0.06 }	0.12	<0.1	—
Uranium .. ..	0.17 } 0.15 }	0.16	221 } 226 }	223
Barium .. ..	<0.01	—	9.9 } 10.2 }	10.0
Lanthanum .. ..	0.10 } 0.10 }	0.10	0.85 } 0.90 }	0.88

The figures quoted include, of course, the real amounts of rubidium and caesium impurity in the samples so they only represent an upper limit on the "apparent" amounts of alkali metals that have been produced. With these figures and the abundances of the elements under consideration in rocks and stony meteorites, the extent of possible errors in alkali-metal determinations in this type of sample that can arise from unwanted nuclear reactions, can be determined. The figures are given in Table XII and show the errors to be quite negligible for all samples that have been examined.

TABLE XII

MAXIMUM ERRORS POSSIBLE IN THE DETERMINATION OF CAESIUM AND RUBIDIUM IN ROCKS AND STONY METEORITES DUE TO UNWANTED NUCLEAR REACTIONS

Element	Igneous rocks		Stony meteorites	
	Average concentration of element,* p.p.m.	Error possible in determination of alkali-metal content, p.p.m.	Average concentration of element,* p.p.m.	Error possible in determination of alkali-metal content, p.p.m.
Strontium ..	300	$2 \times 10^{-4}$ of Rb	20	$1 \times 10^{-5}$ of Rb
Yttrium ..	28.1	$3 \times 10^{-6}$ of Rb	4.7	$6 \times 10^{-7}$ of Rb
Uranium ..	4	$6 \times 10^{-7}$ of Rb $9 \times 10^{-4}$ of Cs	0.36	$6 \times 10^{-8}$ of Rb $8 \times 10^{-5}$ of Cs
Barium ..	250	$2.5 \times 10^{-3}$ of Cs	6.9	$7 \times 10^{-5}$ of Cs
Lanthanum ..	18.3	$2 \times 10^{-5}$ of Cs	1.58	$1 \times 10^{-6}$ of Cs

\* From Rankama and Sahama.<sup>21</sup>

### CONCLUSIONS

The method described in this paper has been applied to samples containing as little as  $6 \times 10^{-9}$  g of rubidium and  $1 \times 10^{-9}$  g of caesium, which, allowing for chemical yields and decay of the rubidium before counting, approaches the limit of detection of the method. At the other end of the scale samples containing as much as 1 mg of rubidium and 1.3 mg of caesium have also been examined. For amounts greater than  $2 \mu\text{g}$  of either alkali metal in the sample, the coefficient of variation is 2 per cent. or less for the rubidium results and less than 3 per cent. for caesium results. Below an estimated  $2 \mu\text{g}$  of alkali metal the precision becomes progressively worse. All of the many products that have been examined have been found to be radiochemically pure.

Making allowance for possible errors in standards, differences in weight between standards and samples for counting, etc., it seems likely that the results quoted for samples containing 10 p.p.m. or more of either alkali metal are within  $\pm 5$  per cent. of the absolute value, and possibly nearer. Certainly the rubidium results that can be reliably compared with those obtained by other workers using other methods (see Tables VII and VIII) tend to confirm this statement. A possible explanation for larger differences, which can be seen in Table VI, for example, for lepidolite A110, may be inhomogeneity of the samples.



The present method supplies an alternative to the method of isotope-dilution analysis for the determination of traces of rubidium and an alternative to isotope dilution and other methods for the determination of rubidium in rubidium minerals. For caesium determinations no method of equal sensitivity is available. The method is a refinement of the procedure described by Cabell and Thomas<sup>11</sup> and refines and extends the scope of that described by Smales and Salmon<sup>10</sup> to cover most materials of geochemical interest.

We thank those who, as mentioned above, have supplied us with samples and the results of their own analyses. We are also grateful to Mr. A. M. Thomas of this establishment, for his assistance in analysing samples.

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October 4th, 1956

## A 250-megacycle High-frequency Titrimeter\*

By E. S. LANE

The design and construction of a stable high-frequency titrimeter operating at 250 Mc/s are described. Examples are given of its use in conventional titrimetric procedures and indications are given of its potentialities in complexometric titrations and in a number of new analytical procedures, e.g., a direct titrimetric determination of potassium as the tetraphenylboron salt and a non-aqueous titrimetric determination of mercury as copper propylenediamine mercuric tetraiodide.

ONE of the chief limitations to the more extensive use of high-frequency titrimetric methods in analytical chemistry lies in the inability of most of the instruments described to operate with solutions containing electrolyte at even moderate concentrations. Theoretical considerations<sup>1</sup> have shown that the sensitivity of high-frequency titrimeters falls off rapidly when the electrolyte concentration in the titration vessel rises above a certain value and that the maximum tolerable electrolyte concentration is directly proportional to the frequency at which the circuit is worked. Whereas an instrument working at 30 Mc/s can be used to titrate solutions of approximately 0.06 *N* sodium chloride (or its equivalent), a 350 Mc/s

\* Presented at the XVth International Congress on Pure and Applied Chemistry (Analytical Chemistry), Lisbon, September 8th to 16th, 1956.

circuit is required to deal with solutions of 0.7 *N* sodium chloride or its equivalent. To date the number of instruments described operating at these higher frequencies is few. Blaedel and Malmstadt used a 350-Mc/s quarter-wavelength concentric-line oscillator, but stated that extreme care in layout of parts and mechanical construction of their instrument was essential in order to reproduce the performance.<sup>2</sup> Johnson and Timnick<sup>3</sup> have described a more simply constructed half-wavelength coaxial-line oscillator operating at 130 Mc/s, but, as both these units are used in conjunction with expensive ancilliary equipment, it was thought that a less expensive instrument in this higher frequency range would be of use in furthering the wider application of high-frequency titrimetry. Accordingly, the design and construction of a simple and stable titrimer working at 200 to 250 Mc/s, reasonably free from critical dimensions and made from readily available inexpensive components, is presented. No difficulty has been experienced in building a number of these units.

The titrimer is developed from an oscillator designed at Oak Ridge for the measurement of concentrations of alkali in aqueous solution and is based on a parallel-transmission-line oscillator, in which a type-955 acorn triode with constant current control of the oscillator plate current is used. The development of this oscillator has been fully described by Stelzner and Kelley.<sup>4</sup>

EXPERIMENTAL

DESCRIPTION OF APPARATUS—

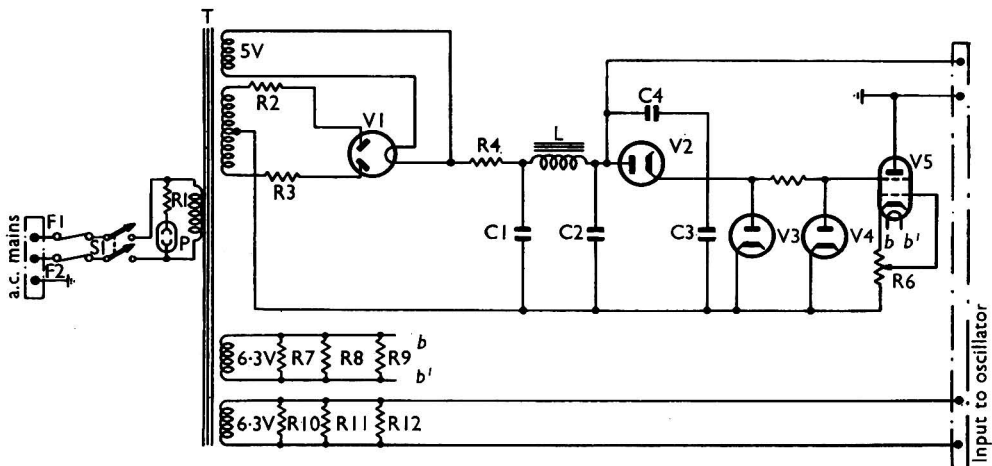


Fig. 1. Circuit for power unit (for values of components, see Appendix, p. 414)

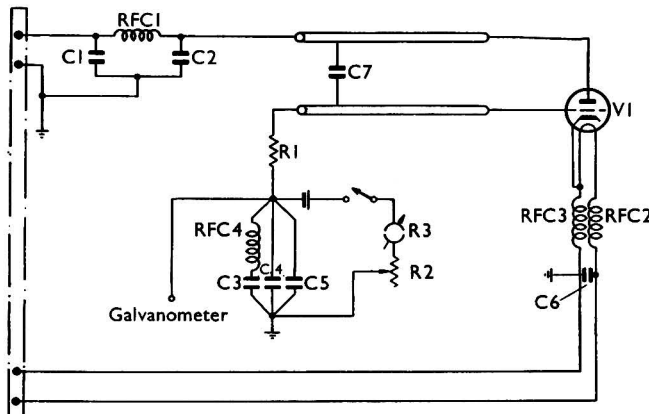


Fig. 2. Circuit for 240-Mc/s oscillator (for values of components, see Appendix, p. 414)

The circuits of the power unit and of the instrument are shown in Figs. 1 and 2, respectively, and the general appearance of the apparatus is seen from Figs. 3 and 4.

*Oscillator*—The parallel-transmission-line oscillator makes use of an RCA 955 acorn triode. Two parallel 8-inch lengths of  $\frac{1}{8}$ -inch copper tubing, spaced  $\frac{3}{4}$  inch apart, are soldered to the plate and grid pins of the valve holder. These lines run vertically in the housing between plastic formers, while rigidly mounted between them is placed the titration vessel. A shorting condenser is soldered in place along the lines so as to establish a suitable oscillating frequency (200 to 250 Mc/s). The cathode and filaments of the valve are isolated from radio-frequency ground by 2 radio-frequency chokes, which are essential to the operation of the oscillator at this frequency because they ensure that the inter-electrode capacities of the valve are part of the tank circuit. Another radio-frequency filter array keeps stray voltages from the power supply. A portion of the grid voltage developed by the oscillator is filtered and fed through a zero-set circuit to a galvanometer. The zero-set circuit consists of a variable potentiometer for coarse control, and a 10-turn helically wound potentiometer for fine adjustment, in series with a large-capacity bell-type dry cell.

*Power supply*—A conventional power supply with full-wave rectification and capacitor-input filtering is used. The design is due to Stelzner and Kelley, modified for British voltages and components.

*Housing*—The power supply is housed in a standard rack unit. The oscillator, titration vessel and zero-set circuit, including the dry cell, are mounted in a 12-inch  $\times$  6 $\frac{1}{2}$ -inch  $\times$  6 $\frac{1}{2}$ -inch aluminium box, which is rigidly bolted to the rack unit. The titration vessel is shielded and connected to earth to avoid stray hand capacitance effects.

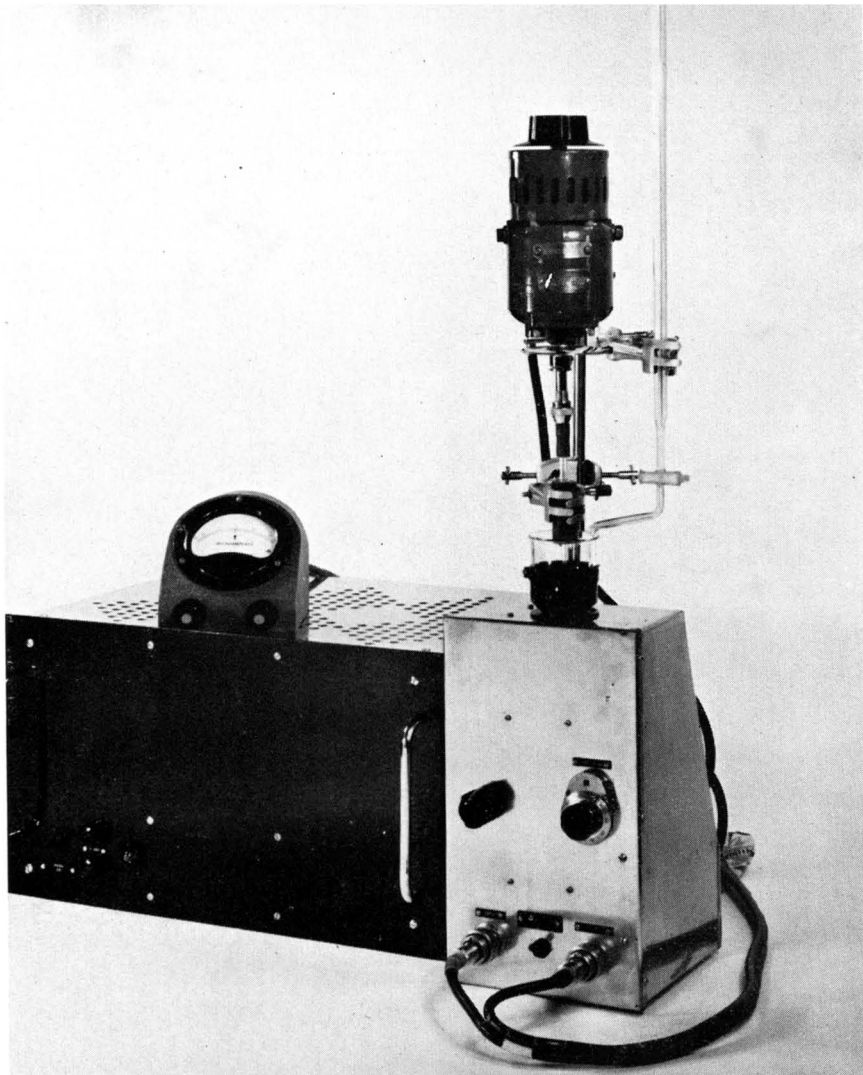
*Titration vessel*—A Pyrex-glass tube,  $\frac{3}{8}$  inch diameter  $\times$  8 inches long, flared out at the upper end for a distance of 1 $\frac{1}{2}$  inches to a diameter of 2 inches is used. This has a working capacity of about 60 ml and the level of the liquid is maintained about 1 inch above the transmission lines, so that changes in liquid level during titration do not affect the response of the instrument. Slightly shorter tubes (6 inches long, and having a capacity of 40 ml) have been used in the more sensitive concentration ranges to achieve more rapid mixing. The cell is rigidly fixed to the chassis and is emptied by means of a suction tube. An electrically driven stirrer, comprising a 6-inch  $\times$   $\frac{1}{4}$ -inch  $\times$   $\frac{1}{8}$ -inch glass strip, twisted longitudinally through 360° and fixed to a glass rod, is required to mix the solution during titration.

*Stability*—The designers of this oscillator showed it to have a remarkable stability, which develops after a warm-up period of about half an hour. When the titration vessel is filled with a conducting liquid, the absorption of radio-frequency energy results in a rise in the temperature of the solution and, since the conductivity of the solution is temperature dependent, this absorption of energy leads to some instability. When the cell was filled with water (50 ml), the temperature rise amounted to 3.5° C per hour from a room temperature of 20° C. Since a titration requires only 10 minutes at most for completion, this effect is negligible for most practical purposes.

A further example of the temperature dependence of conductivity interfering with titration occurred when concentrated solutions of acids and bases (2 *N*) were being titrated during the preliminary investigation of the performance of the instrument. The heat of reaction was sufficient to cause a departure from linearity of the titration curves. However, this concentration of titrants is rarely encountered and dilution before titration minimises this complication.

#### RESPONSE CURVES—

Some idea of the performance of the instrument can be obtained from Fig. 5, in which the response of the instrument to progressively increasing concentrations of sodium chloride is plotted. Although Fig. 5 indicates that the instrument can still detect concentration changes at a concentration level of 60 to 70 g of sodium chloride per litre, it should be remembered that this is a null instrument and that the movement of the galvanometer needle from zero and its return by means of the zero-set circuit are highly damped at these high ionic concentrations. Here, a change in concentration causes a relatively slight divergence of the galvanometer needle from zero and its return by means of the zero-set circuit requires a relatively large movement of the potentiometer compared with the restoration of the same divergence at a lower ionic concentration. With high concentrations of electrolyte, therefore, the accuracy with which the potentiometer can be read is markedly dependent on the sensitivity of the galvanometer.



**Fig. 3.** View of high-frequency titrimeter

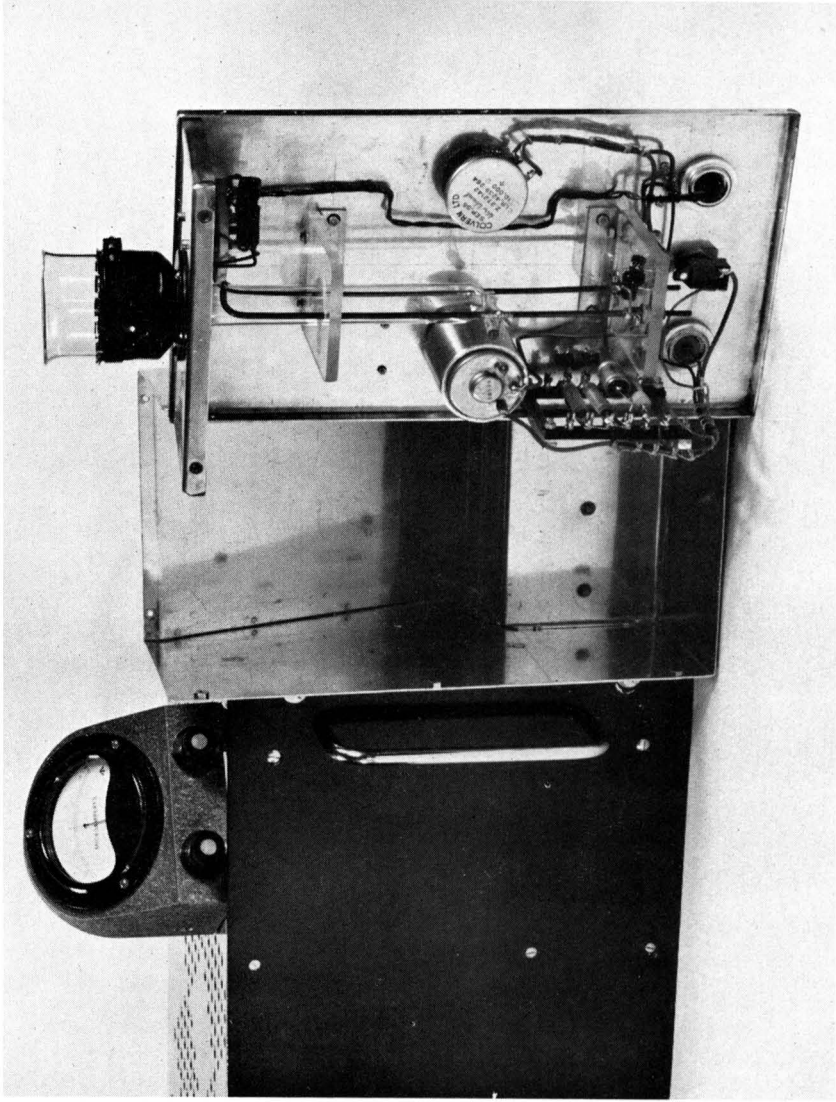


Fig. 4. View of high-frequency titrimeter, showing layout of components

Stelzner and Kelley point out that with an oscillator of this type the change in conductivity of the solution in the cell contributes a greater share to the change in oscillator response than the change in dielectric constant. They found with potassium hydroxide solutions a close relationship between oscillator response and specific conductance.

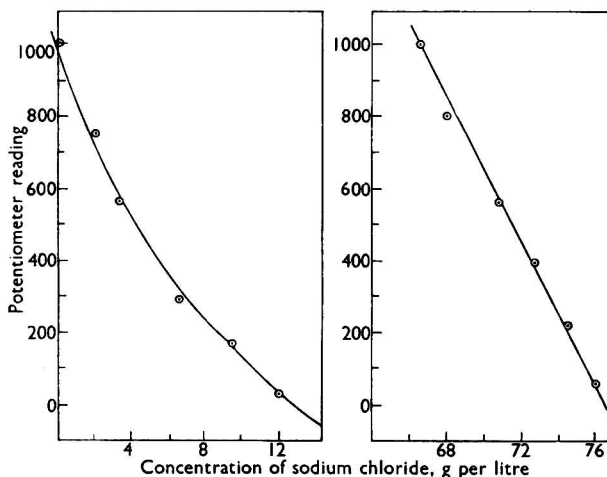


Fig. 5. Response curves with the 250-Mc/s titrimer

#### METHOD OF USE—

The method of operation of the instrument is similar to that used by Lane<sup>5</sup> for the instrument designed by Dowdall, Sinkinson and Stretch.<sup>6</sup> The solution to be titrated is placed in the titration cell and diluted to the required volume. The stirrer is started and the galvanometer current adjusted to zero. Additions of titrant are made, the galvanometer being adjusted to zero after each addition and the scale reading recorded on the helically wound potentiometer. As the end-point is approached, there is a change of slope of the plot of potentiometer scale readings against volume of titrant added. Frequently a complete reversal of slope occurs. As is customary with many instrumental titrations, it is generally advantageous to determine the end-point approximately with large increments of titrant and then to carry out a duplicate titration with small increments in the vicinity of the end-point.

#### APPLICATIONS OF THE HIGH-FREQUENCY TITRIMETER

##### ACID - BASE AND ARGENTIMETRIC TITRATIONS—

Fig. 6 shows the end-point obtained in the titration of aqueous hydrochloric acid with *N* sodium hydroxide. The same end-point is obtained when the solution is "loaded" with inert electrolyte, but then slope of the approach and retiring lines are reversed. This reversal of slope with differing ion concentrations has been noted by other workers.

Fig. 7 shows the type of curve obtained when a solution of 0.1 *N* silver nitrate is titrated with 0.1 *N* potassium chloride.

The end-points in these titrations agreed excellently with those obtained by well established methods.

##### TITRATIONS IN NON-AQUEOUS SOLVENTS—

Considerable progress has been made in the application of high-frequency conductimetric methods to non-aqueous titrimetry. Wagner and Kauffman<sup>7</sup> used the technique for the titration of bases in glacial acetic acid, and acids in dimethylformamide were titrated with sodium methoxide by Dean and Cain.<sup>8</sup> My experience<sup>5</sup> of high-frequency titrimetry with a wide variety of compounds, including phenols, enols, quaternary ammonium salts and heterocyclic bases, suggests that the method is comparable in performance to the potentiometric determination, but is far more convenient in operation.

The examination of several representative titrations in glacial acetic acid, ethylenediamine and dimethylformamide with this titrimer has indicated, however, that no advantage is to be gained by performing these titrations at frequencies greater than 15 Mc/s.

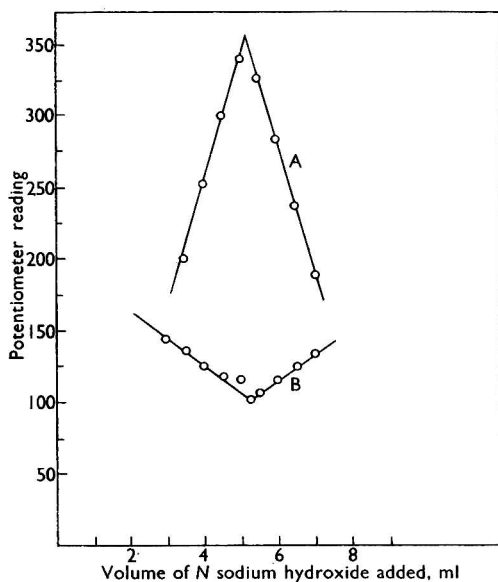


Fig. 6. Acid - base titration; curve A, hydrochloric acid titrated with *N* sodium hydroxide; curve B, hydrochloric acid titrated with *N* sodium hydroxide in presence of 5 ml of 10 per cent. w/v potassium chloride. Indicator end-point, 5.2 ml; volume at end-point, 40 ml

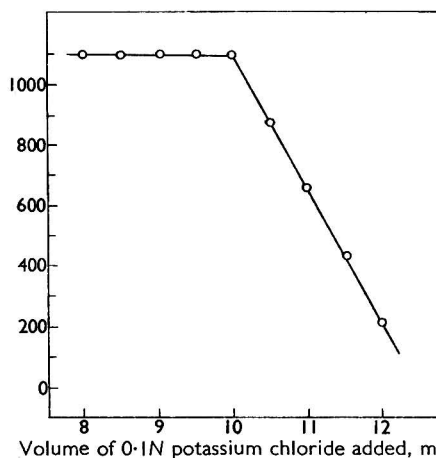


Fig. 7. Argentimetric titration, 10 ml of 0.1 *N* silver nitrate being titrated against 0.1 *N* potassium chloride

#### HIGH-FREQUENCY CONDUCTIMETRIC DETERMINATION OF POTASSIUM BY DIRECT TITRATION WITH SODIUM TETRAPHENYLBORON—

The quantitative determination of potassium is one of the less satisfactory analytical procedures and the method at present in vogue is based on its gravimetric determination as potassium tetraphenylboron. Various attempts have been made to devise volumetric methods based on the formation of the potassium tetraphenylboron precipitate, but apart from the conductimetric titration of Raff and Brotz,<sup>9</sup> in which the titrant is used as the precipitant, all the methods involve the prior separation of the precipitate by filtration, and it is precisely this operation that is to be avoided in this particular determination because of the difficult physical form of the precipitate and the careful washing technique required. In view of the fact that Raff and Brotz successfully titrated potassium solutions with lithium or sodium tetraphenylboron solutions and obtained sharp end-points conductimetrically, the high-frequency conductimetric method with its advantages of contactless electrodes was applied to this system and Fig. 8 shows the type of curve obtained. The sodium tetraphenylboron solution (0.1 *N*) was prepared in the usual way and standardised against potassium hydrogen phthalate solution and then used to determine the unknown potassium solution in 0.05 *N* acetic acid. The sodium tetraphenylboron solution may also be standardised against silver nitrate by this method.

In experiments when 8.26 mg of potassium chloride were taken, the recoveries were 8.21, 8.28 and 8.27 mg.

#### NON-AQUEOUS TITRIMETRIC DETERMINATION OF MERCURY (Hg<sup>2+</sup>) FROM AQUEOUS SOLUTIONS—

There are many examples in classical analytical chemistry in which a gravimetric determination of a metal is avoided by allowing a precipitated metal compound (or its solution in a suitable reagent) to react with a standardised titrant in preference to the weighing of

the precipitate itself. Perhaps the most widely used is the bromimetric determination of metal oxinate precipitates.

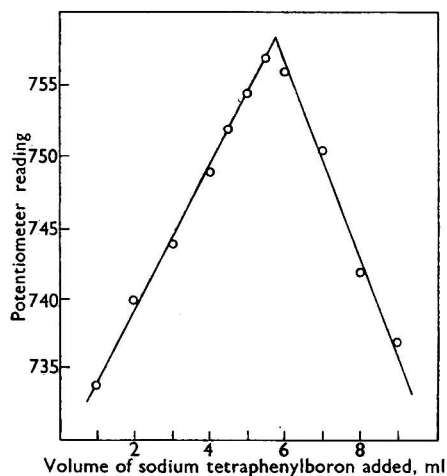


Fig. 8. Determination of potassium by direct titration with sodium tetraphenylboron

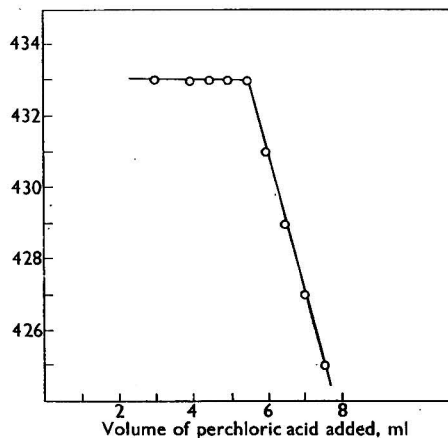


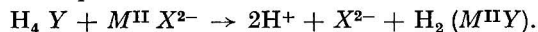
Fig. 9. Determination of mercury ( $\text{Hg}^{2+}$ ) as copper propylenediamine mercuric iodide by titration with perchloric acid in acetic acid. Found, 0.100(4) g of  $\text{Hg}^{2+}$ ; taken, 0.1004 g of  $\text{Hg}^{2+}$

The increasing use of titrations in non-aqueous solvents greatly widens the scope of the "titrimetric" finish to the quantitative determination of metals, and a notable example in recent years of the use of this particular method has been the titration by Flaschka of potassium tetraphenylboron precipitates with perchloric acid in glacial acetic acid with a visual indicator. An example of the use of a high-frequency titrimetric finish in a conventional determination of a heavy metal is provided by a modification of the method of Spacu and Spacu<sup>11</sup> for mercuric ions. The metal is precipitated from aqueous solution by the addition of potassium iodide and cupric propylenediamine sulphate as  $\text{Cu.pn}_2.\text{HgI}_4$  ( $\text{pn} = 1:2$ -propanediamine). This precipitate can be dissolved in glacial acetic acid and mercuric acetate and titrated with perchloric acid in glacial acetic acid, four equivalents of perchloric acid, a very favourable volumetric factor, being required for equivalence. The mercuric acetate is required for the conversion of iodide ion to acetate ion (see Pifer and Wollish<sup>12</sup>). Conventional visual indicators for this particular titration, *e.g.*, Oracet blue B and crystal violet, give indistinct end-points, but Fig. 9 shows the highly satisfactory end-point given with this titrimeter. The precipitation and washing of the mercury precipitate was carried out as described by Walton and Smith,<sup>13</sup> except that the precipitate, without being dried, was dissolved in glacial acetic acid and mercuric acetate and titrated with 0.1 *N* perchloric acid in glacial acetic acid.

#### THE STUDY OF CHELATION—

*Compleximetric titrations*—Chelation may be profitably studied by means of high-frequency titrimetry. As ethylenediaminetetra-acetic acid (EDTA) is one of the strongest and most generally applicable chelating agents in use, some examples of the use of this technique in the study of EDTA and related compounds are presented.

The analytical use of EDTA-type compounds is usually based either on the measurement of hydrogen ion released during chelation or on the direct measurement of the compleximetric reaction itself. A general equation for the reaction with a metal salt is—



The drop in pH due to liberation of the hydrogen ion may be determined by titration with alkali. Alternatively, the end-point of the compleximetric reaction may be indicated by potentiometric, amperometric, spectrophotometric or internal-indicator methods. Suitable indicators for the last method comprise those compounds forming coloured weakly bound complexes with the ion being titrated.



Considerable impetus has been given to the use of high-frequency titrimetry in the study of these reactions by the work of West<sup>14</sup> and his school at the Louisiana State University. The results obtained by these workers with the Sargent Oscillometer can be repeated by using the 250-Mc/s titrimer in a much higher ionic concentration.

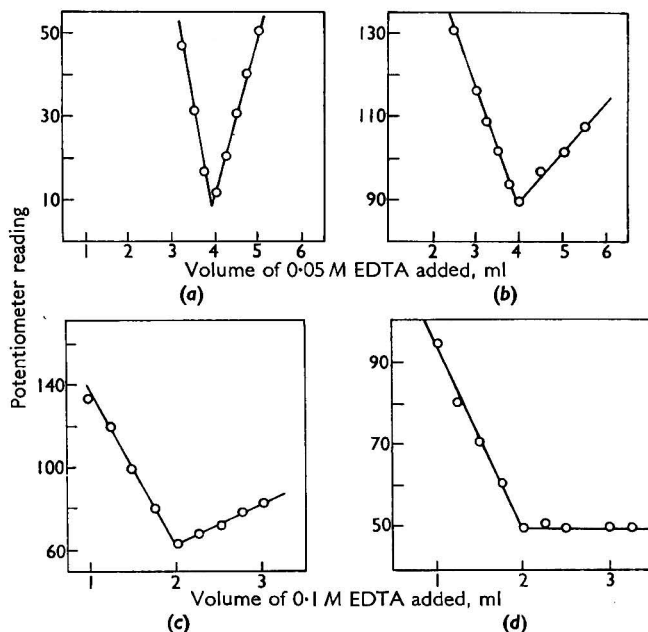


Fig. 10. Titration of thorium with EDTA: (a), 5 ml of 0.04 *M* thorium nitrate; (b), as (a) with 10 ml of 0.1 *N* potassium chloride added; (c), as (a) with 5 ml of 0.1 *N* sulphuric acid added; (d), as (a) with 0.25 g of ammonium sulphate added

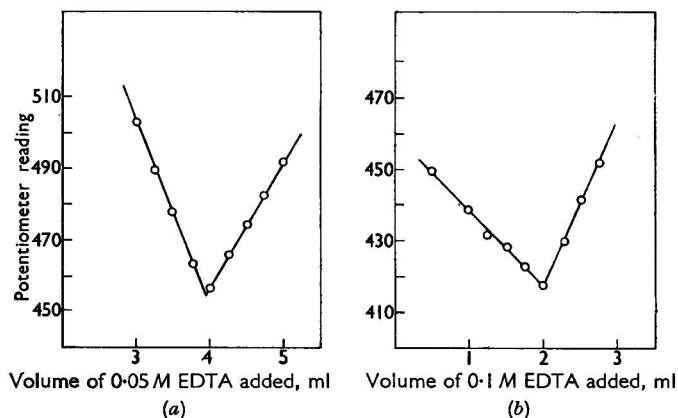


Fig. 11. Titration of thorium with EDTA: (a), 5 ml of 0.04 *N* thorium nitrate and 2.5 ml of 0.1 *N* silver nitrate; (b), 5 ml of 0.04 *N* thorium nitrate and 0.5 ml of glacial acetic acid

Fig. 10 shows the titration of thorium with EDTA (disodium salt). In the main the results obtained by Hara and West<sup>14</sup> have been substantiated. It is confirmed that thorium forms a (1 + 1) complex with EDTA and that sulphate ion does not mask the high-frequency conductimetric determination. But, whereas Hara and West found serious interference by

acetate ion, Fig. 11 shows a satisfactory titration of thorium by EDTA in the presence of a large excess of acetate ions. By using this technique similar (1 + 1) complexes have been observed for thorium and diethylenetriaminepenta-acetic acid and *cyclohexyl-1:2-diamine-tetra-acetic acid*.

Fig. 12 shows a titration of the monosodium and disodium salts of nitrilotriacetic acid (NTA) titrated with a standard solution of copper and indicates the relatively high ionic concentrations that can be satisfactorily dealt with by this instrument.

*Chelating agents in non-aqueous titrimetry*—Some of the limitations of the use of chelating agents for the titrimetric determination of metals are due to the following causes—

- (i) the chelating agent does not combine with the metal ion sufficiently strongly to give a good titration curve, and
- (ii) intermediate compounds formed between the metal ion and the chelating agent mask the titration curve

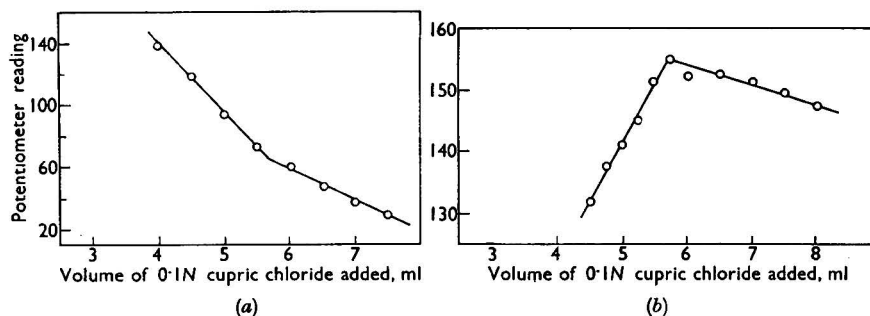


Fig. 12. Titration of NTA with copper: (a), 0.1 g of NTA and 10.5 ml of 0.1 N sodium hydroxide; (b), 0.1 g of NTA and 21.0 ml of 0.1 N sodium hydroxide

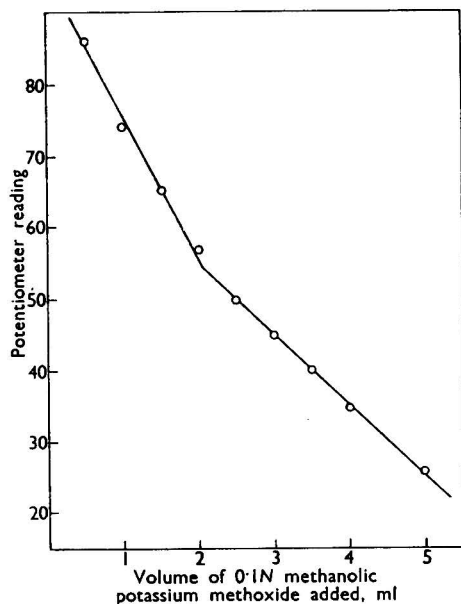


Fig. 13. Uranyl nitrate - sodium salicylate chelation in methanol

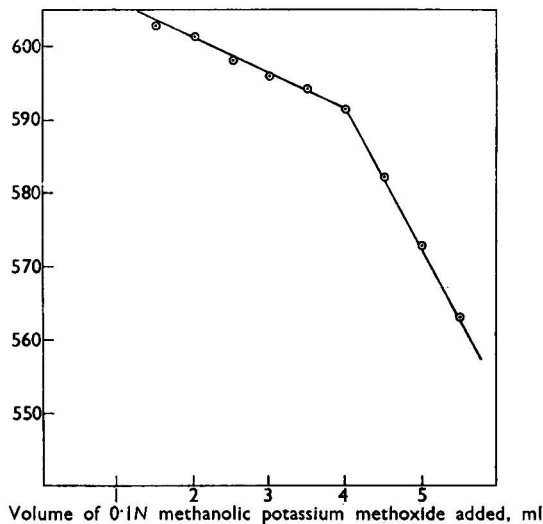


Fig. 14. Uranyl nitrate - 8-hydroxyquinoline chelation in methanol

The use of non-aqueous media for these titrations, introduced by Brummett and Hollweg,<sup>15</sup> marks a considerable forward step in this field, since the choice of chelating agents is widened (many are insufficiently soluble in water for use in aqueous systems) and the formation constant may be favourably altered.

The high-frequency conductimetric-titration technique has been applied to these systems in view of my conviction that this method is simpler than the conventional potentiometric end-point detection, particularly in inexperienced hands. This method has been applied to the determination of uranyl ion by means of sodium salicylate. An excess of solid sodium salicylate was added to an aliquot of uranyl nitrate solution (0.1 *N*) and the solution was diluted to the required volume (40 ml) with methanol. Hydrogen ion is released during the chelation and this is titrated with standardised potassium methoxide in a benzene-methanol mixture. Fig. 13 shows the titration curve, which is of some theoretical importance in so far as it proves that the *o*-hydroxyl group of salicylic acid is displaced during the chelation process, whereas Bernstrom,<sup>16</sup> working on the basis of the similarity between salicylic acid and *o*-methoxybenzoic acid in extraction experiments, concluded that only the carboxyl group was involved with the uranyl ion.

Fig. 14 shows a similar titration; uranyl nitrate in methanol is treated with an excess of 8-hydroxyquinoline and the hydrogen ion released during chelation is titrated with potassium methoxide in a benzene-methanol mixture.

## APPENDIX

### LIST OF COMPONENTS USED IN THE CONSTRUCTION OF THE POWER UNIT

(Fig. 1)

R <sub>1</sub>	= 470,000-ohm, $\frac{3}{4}$ -watt, carbon resistance.
R <sub>2</sub> , R <sub>3</sub>	= 1200-ohm, 3-watt, wire-wound resistance.
R <sub>4</sub>	= 100-ohm, 10-watt, wire-wound resistance.
R <sub>5</sub>	= 12,000-ohm, 6-watt, wire-wound resistance.
R <sub>6</sub>	= 2500-ohm, wire-wound variable resistance.
R <sub>7</sub> , R <sub>8</sub> , R <sub>9</sub> , R <sub>10</sub> , R <sub>11</sub> , R <sub>12</sub>	= 10-ohm, 10-watt, wire-wound resistance.
C <sub>1</sub> , C <sub>2</sub>	= 8- $\mu$ F condenser.
C <sub>3</sub> , C <sub>4</sub>	= 0.1- $\mu$ F condenser.
V <sub>1</sub>	= CV 1268 valve.
V <sub>2</sub>	= CV 686 valve.
V <sub>3</sub>	= CV 216 valve.
V <sub>4</sub>	= CV 449 valve.
V <sub>5</sub>	= CV 848 (6 AG 5) valve.
T	= Mains transformer: primary winding, 250 volts; secondary windings, 250-0-250 volts, 5 volts, 6.3 volts and 6.3 volts.
L	= 10-henry 60-mA choke, of d.c. resistance 390 ohms.
P	= Neon indicator.
PL1	= Three-pin small fixed plug (Plessey).
PL2	= Six-pin small fixed socket (Plessey).
F <sub>1</sub> , F <sub>2</sub>	= 2-amp fuse.
S <sub>1</sub>	= Double-pole switch.

### LIST OF COMPONENTS USED IN THE CONSTRUCTION OF THE OSCILLATOR

(Fig. 2)

R <sub>1</sub>	= 25,000-ohm resistance, with a 2 per cent. tolerance.
R <sub>2</sub>	= 10,000-ohm potentiometer.
R <sub>3</sub>	= 1000-ohm helical wire-wound potentiometer (Colvern).
C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> , C <sub>4</sub> , C <sub>6</sub>	= 0.005- $\mu$ F condenser, with $\pm$ 20 per cent. tolerance.
C <sub>5</sub>	= 0.1- $\mu$ F condenser, with $\pm$ 25 per cent. tolerance.
C <sub>7</sub>	= 820- $\mu$ F condenser.
V <sub>1</sub>	= RCA955 (acorn type).
RFC1, RFC2, RFC3, RFC4	= Radio-frequency choke.

I am indebted to Mr. C. Lomas, A.E.R.E., for the construction of the instrument; to Mr. T. Jaques and Mr. S. J. Burnett, A.E.R.E., for helpful discussions on circuitry and to Dr. J. K. Aiken, Geigy Ltd., who kindly provided a supply of diethylenetriaminepenta-acetic acid and cyclohexyl-1 : 2-diaminetetra-acetic acid.

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## CHEMISTRY DIVISION

ATOMIC ENERGY RESEARCH ESTABLISHMENT  
HARWELL, NR. DIDCOT, BERKS.

October 12th, 1956

## Polarographic Determinations of Thorium

BY R. P. GRAHAM AND G. B. LARRABEE\*

Indirect polarographic methods for the determination of thorium are described. These depend on the precipitation of thorium by either *m*-nitrobenzoic acid, *m*-nitrophenylarsonic acid or 8-hydroxyquinoline, the dissolution of the separated and washed compound, and then the polarographic determination of the regenerated organic reagent. The pH conditions required for the precipitations by the reagents and appropriate for their polarographic determination are discussed. The method with *m*-nitrobenzoic acid, in which thorium is precipitated as the tetra-(*m*-nitrobenzoate), has been shown to be applicable to the determination of thorium in magnesium alloys containing zinc and rare-earth elements.

In the last few years much study has been made of methods for the determination of thorium. New absorptiometric, titrimetric, gravimetric, spectrochemical, and X-ray fluorescence methods, amongst others, have been developed since Moeller, Schweitzer and Starr<sup>1</sup> published their review of the analytical chemistry of thorium in 1948. Very little attention, however, has been given to polarographic methods.

Thorium apparently cannot be determined by a direct polarographic method, the value of its half-wave potential being too negative to permit the recording of a wave before hydrogen ions or other cations of the supporting electrolyte are reduced.<sup>2</sup> One indirect polarographic method has been developed, by Komárek.<sup>3</sup> This depends on the polarographic determination of iodate after converting, by means of sodium hydroxide, a precipitate of thorium iodate to one of hydrous thoria. Associated with this method is the difficulty of freeing precipitated thorium iodate from adsorbed iodate without the loss of significant amounts of thorium by dissolution and hydrolysis<sup>4</sup> and, further, the difficulty of washing the desired iodate out of a precipitate of hydrous thoria.

This paper describes indirect polarographic methods for thorium in which use is made of an organic reagent both as a precipitant and as a polarographically reducible substance. *m*-Nitrophenylarsonic acid, 8-hydroxyquinoline and *m*-nitrobenzoic acid have been studied, and it has been shown that each of these can be the basis of a precise and accurate polarographic method for thorium. The methods involve the quantitative precipitation of thorium, under controlled conditions, by the organic reagent, then the dissolution of the separated and washed precipitate, and finally the polarographic determination of the free organic reagent that results from the dissolution. By appropriate calibration procedures,

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the amount of the organic reagent that is found is related to the amount of thorium in the original solution. Of the three reagents, *m*-nitrobenzoic acid is the most useful (*vide infra*).

The organic reagents with which this paper is concerned have been used in other studies of the analytical chemistry of thorium. *m*-Nitrophenylarsonic acid has been proposed for use in an amperometric titration of thorium<sup>5</sup>; 8-hydroxyquinoline has been used for the determination of thorium by gravimetric and titrimetric methods,<sup>1,6</sup> and for the separation of thorium from cerium<sup>7,8,9</sup> and from lanthanum<sup>7</sup>; *m*-nitrobenzoic acid, first proposed as a precipitant for thorium half a century ago,<sup>10</sup> but not given much attention until recently, has lately been used or recommended for the gravimetric determination of thorium,<sup>11,12,13</sup> for the separation of thorium and zirconium<sup>11,12,14</sup> (by control of the pH of precipitation) and as the basis of a titrimetric method<sup>15</sup> and a colorimetric method<sup>16</sup> for thorium.

#### METHOD

##### APPARATUS—

The polarograph was a Tinsley pen-recording instrument, type V722/13. The capillary for the dropping-mercury electrode was a piece of marine barometer tubing. A conventional H-type of polarographic cell<sup>17</sup> was used, electrolytic contact with the saturated calomel reference cell being made through a potassium chloride-agar bridge.

Measurements of pH were made with a Beckman model G pH meter, equipped with a G-1190-80 glass electrode.

##### REAGENTS—

The mercury for the dropping-mercury electrode was purified by washing it for at least 10 hours in 10 to 15 per cent. nitric acid, then washing it several times with water and finally distilling it twice *in vacuo*.

The 8-hydroxyquinoline was AnalaR grade, the *m*-nitrophenylarsonic acid was Eastman white-label grade (obtained from Distillation Products Industries, Rochester, U.S.A.), and the *m*-nitrobenzoic acid was prepared by the method described by Kamm and Segur.<sup>18</sup>

The magnesium was metal that had been specially purified by sublimation (obtained from Dow Chemical Co., Midland, U.S.A.), and the mischmetal (obtained from Dominion Magnesium Ltd., Haley, Canada) was stated to contain  $45 \pm 1$  per cent. of cerium, 97 per cent. of total rare-earth elements, 3 per cent. of iron and 0.004 per cent. of thorium. The alizarin blue was a spot-test reagent grade (obtained from British Drug Houses Ltd.) and the gelatin was purified Pigskin Gelatin (obtained from Eastman Kodak Co., Rochester, U.S.A.).

A purified sample of thorium tetrachloride was obtained as follows. A hot saturated aqueous solution of a C.P. commercial product (obtained from Amend Drug and Chemical Co., New York, U.S.A.) was prepared and allowed to cool at room temperature; the solution was saturated with hydrogen chloride and an equal volume of ethyl ether was added; the mixture was shaken until crystallisation was complete, and then it was filtered and the product was washed several times with ether. The purified salt was dried at room temperature *in vacuo*. Stock solutions of thorium chloride in 5 per cent. hydrochloric acid (about 2 mg of thorium per ml) were prepared and their thorium contents were determined by precipitation of the hydrous oxide by means of ammonia solution, followed by ignition to thorium dioxide. Thorium solutions for calibration work and other purposes were obtained, as needed, by quantitatively diluting a stock solution with water.

All other reagents were of recognised analytical quality.

##### POLAROGRAPHIC PROCEDURES—

Before polarograms were recorded, each solution was de-aerated by bubbling through it for 10 minutes nitrogen that had been purified by being passed through a solution of pyrogallol in aqueous potassium hydroxide and then through water.

All polarographic measurements were made at  $25.0^\circ \pm 0.05^\circ$  C. Usually five polarograms for each solution were recorded, and the average wave height was taken as the value.

#### THORIUM 8-HYDROXYQUINOLATE

##### POLAROGRAPHY—

Although the behaviour of 8-hydroxyquinoline at the dropping-mercury electrode is complicated and pronouncedly dependent on pH,<sup>19,20</sup> this reagent has found polarographic applications in inorganic analysis. Magnesium and aluminium, for example, have been

determined indirectly, by the measurement of one of the waves given by this reagent, at a controlled pH, after dissolution of the precipitated metal 8-hydroxyquinolate (or by measurement of the excess of reagent after precipitation). Different media of differing pH have been recommended for the polarographic determination of 8-hydroxyquinoline: Caruthers<sup>21</sup> used a phosphate buffer of pH 7.1; Stone and Furman,<sup>22</sup> an ammonia - ammonium chloride buffer of pH 10; Parks and Lykken,<sup>23</sup> the same buffer system at pH 9.8. We have obtained very satisfactory results in a phosphate buffer at pH 12.0 (disodium monohydrogen phosphate, 0.10 *M*, and sodium hydroxide, 0.10 *M*). Under these conditions, 8-hydroxyquinoline gives a single and well formed wave in the presence of gelatin as a maximum suppressor. The diffusion current given by 8-hydroxyquinoline is linearly related to the amount of thorium (at least up to 10 mg) that was present in the solution from which it was precipitated by the organic reagent, the procedure described in detail below being used.

#### PRECIPITATION—

Whether the precipitate that thorium gives with 8-hydroxyquinoline contains 4 or 5 moles of the organic reagent for every mole of thorium depends on the temperature of precipitation.<sup>24</sup> (Scandium, uranium, and plutonium also form 8-hydroxyquinolates with an "extra" molecule of the organic reagent.<sup>25</sup>) The structure of the "5-complex" of thorium has been the subject of recent investigations.<sup>7,24</sup>

We have found that homogeneous precipitation of thorium 8-hydroxyquinolate by means of urea yields a precipitate that coagulates more rapidly and that is more easily filtered off and washed than that obtained by the method of Frere.<sup>26</sup> (Moeller and Ramaniah<sup>24</sup> also recommend a homogeneous precipitation of this compound.) On the basis of its colour and the temperature of its precipitation, the 8-hydroxyquinolate that we obtained can be presumed to be the "5-complex."

#### PROCEDURE—

To 50.0 ml of a thorium solution containing about 10 mg of thorium there were added, drop by drop, 8 *M* sodium hydroxide until hydrous oxide just succeeded in re-dissolving on stirring, then 10 ml of a 2.5 per cent. solution of 8-hydroxyquinoline in 1.0 *M* acetic acid and finally 12 g of urea. The solution was heated and kept just below the boiling point for about 20 minutes, until the orange-red precipitate, which forms on hydrolysis of the urea, coagulated. The precipitate was collected on a Whatman No. 42 filter-paper and washed thoroughly with water. Next, the precipitate was dissolved directly into a 100-ml calibrated flask by means of hot 6 *M* hydrochloric acid. Five millilitres of a 20 per cent. solution of tartaric acid were then added (to complex the thorium so that it would not be re-precipitated during the subsequent adjustment of the pH of the solution for polarography), and, by using 8 *M* sodium hydroxide, the pH of the solution was brought to the end-point of alizarin blue. Finally, a further 2 ml of 8 *M* sodium hydroxide, 35 ml of a 0.10 *M* disodium monohydrogen phosphate - 0.10 *M* sodium hydroxide buffer solution of pH 12.0 and 1 ml of a 0.75 per cent. aqueous gelatin dispersion were added, and the solution was diluted to volume with water and polarograms were recorded.

A procedure that obviates any treatment of the thorium 8-hydroxyquinolate consists in adding an exactly known volume of the solution of 8-hydroxyquinoline and polarographically determining the excess of the organic reagent in the filtrate. With concentrations of reagents slightly different from those given above, and omitting the tartrate (since there is no thorium in need of complexing), this indirect approach has been shown, like the one above, to yield a straight-line calibration curve for amounts of thorium up to at least 10 mg. Procedures similar to this have been recommended for the polarographic determination of magnesium<sup>22</sup> and of aluminium.<sup>23</sup>

#### THORIUM *m*-NITROPHENYLARSONATE

##### POLAROGRAPHY—

A tracing of the excellent polarographic wave that *m*-nitrophenylarsonic acid can give at pH 4.0 in a solution of potassium hydrogen phthalate (with methyl red as a maximum suppressor) is shown in another paper from this laboratory.<sup>27</sup> The diffusion current given by this arsonic acid was found to be a linear function of the amount of thorium (at least up to 20 mg) that was present in the solution from which it was precipitated (at a pH of 1.9 ± 0.1, by the procedure given below).

## PRECIPITATION—

The extent to which thorium is precipitated by *m*-nitrophenylarsonic acid depends on the pH of the solution, as is shown in Fig. 1. Each point on the curve for thorium *m*-nitrophenylarsonate was obtained as follows. To 50.0 ml of a thorium tetrachloride solution, containing about 10 mg of thorium, there was added 4 *M* ammonia solution until the desired pH value was reached and then 50 ml of a 0.24 per cent. aqueous solution of *m*-nitrophenylarsonic acid of the same pH. The precipitate was kept at room temperature for 2 hours to coagulate it, then it was collected on a Whatman No. 42 filter-paper and washed four times with water. Next, the precipitate was dissolved directly into a 100-ml calibrated flask by means of a hot tartrate solution (prepared by making a 0.5 *M* solution of tartaric acid strongly alkaline to phenolphthalein with concentrated sodium hydroxide), and the pH of the solution was adjusted to the methyl red end-point with 5 *M* perchloric acid. Thirty-five millilitres of a saturated potassium hydrogen phthalate solution were added (as buffer and supporting electrolyte), and the solution was diluted to volume with water and polarograms were recorded.

From curve A, Fig. 1, it is clear that, from hydrochloric acid solutions, thorium gives no precipitate with *m*-nitrophenylarsonic acid at a pH below 0.7, and an analytically useful *m*-nitrophenylarsonate precipitate only in the pH range 1.4 to 2.6. At higher pH values the precipitate is a mixed one, presumably of arsonate and hydrous oxide. Similar findings have been reported for titanium *m*-nitrophenylarsonate.<sup>27</sup>

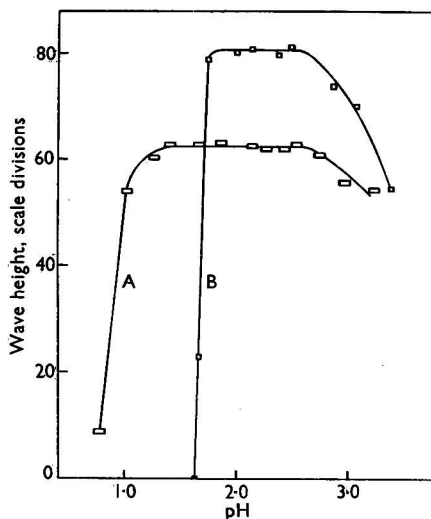


Fig. 1. Effectiveness of *m*-nitrophenylarsonic acid (curve A) and *m*-nitrobenzoic acid (curve B) as precipitants for thorium as a function of pH. The amount of thorium was constant throughout the experiments represented by curve A, and likewise for curve B, although it was somewhat different in the two instances

The finding of Kolthoff and Johnson<sup>5</sup> that *m*-nitrophenylarsonic acid can be used for the amperometric titration of thorium in hydrochloric acid when the pH is 2.0 to 2.5, but not when the pH is 1, is of course consistent with the results shown in Fig. 1.

## PROCEDURE—

The recommended procedure is that given in the preceding section, with the thorium solution being first brought to a pH of  $2.0 \pm 0.1$  (or at most  $\pm 0.2$ ) and the *m*-nitrophenylarsonic acid solution being of pH 2.0.

THORIUM *m*-NITROBENZOATE

## POLAROGRAPHY—

The polarographic diffusion current for a given concentration of *m*-nitrobenzoic acid (and also its half-wave potential) depends on the pH of the solution.<sup>28,29</sup> For analytically useful results a good buffer is therefore required, as with 8-hydroxyquinoline and *m*-nitrophenylarsonic acid. We have found that potassium hydrogen phthalate serves well as a buffer (pH 4.0) and as a supporting electrolyte. Under these conditions, and with 0.005 per cent. of 1-naphthol present as a maximum suppressor, *m*-nitrobenzoic acid yields a very well formed and easily measurable wave, such as that shown in Fig. 2. Although *m*-nitrobenzoic acid can yield two waves, only one appears at pH 4.0; this probably corresponds to a reduction of the nitro group to the hydroxylamine stage.

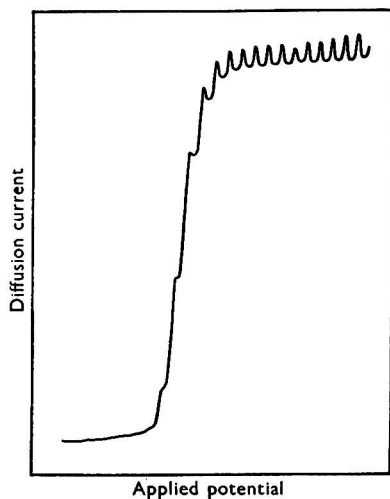


Fig. 2. Typical polarographic wave for the reduction of *m*-nitrobenzoic acid at pH 4.0

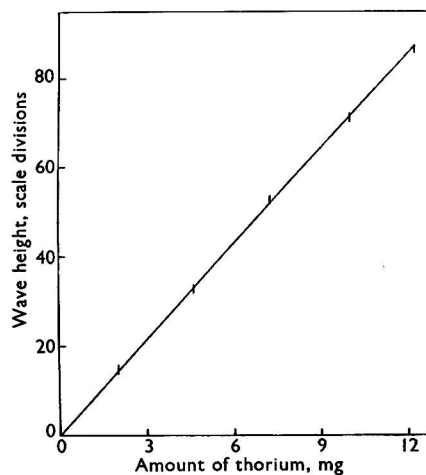


Fig. 3. Diffusion current (wave height) of *m*-nitrobenzoic acid (at pH 4.0) as a linear function of the amount of thorium present in the solution from which it was precipitated (at pH 2.15)

The linear relation between the height of the wave for *m*-nitrobenzoic acid and the amount of thorium present in the solution from which it was precipitated, at pH  $2.15 \pm 0.10$ , is shown in Fig. 3.

## PRECIPITATION—

As with the other organic reagents, the effectiveness of *m*-nitrobenzoic acid as a precipitant for thorium depends on the pH of the solution. Each point on the curve for thorium *m*-nitrobenzoate that is shown in Fig. 1 was obtained as follows. To 50.0 ml of a thorium tetrachloride solution, containing about 10 mg of thorium, there were added 3 to 4 ml of 12 *M* hydrochloric acid, 50 ml of a saturated aqueous solution of *m*-nitrobenzoic acid (see Note 1) and then 7.5 *M* ammonia solution until the desired pH was attained. The precipitate was coagulated by heating the mixture near the boiling point for about 15 minutes, and then was collected on a Whatman No. 40 filter-paper and washed with hot water. Next, the precipitate was dissolved directly into a 100-ml calibrated flask by means of hot 4 *M* perchloric acid (see Note 2). Five millilitres of a 20 per cent. tartaric acid solution were added (see Note 3) and the pH of the solution was adjusted to the methyl red end-point by adding 15 *M* ammonia solution from a burette. Thirty-five millilitres of a saturated solution of potassium hydrogen phthalate were added (as buffer and supporting electrolyte), and then 10 drops of a 1 per cent. solution of 1-naphthol in ethanol (as a maximum suppressor). Finally, the solution was diluted to volume with water and polarograms were recorded.

From curve B, Fig. 1, it is evident that thorium gives no precipitate with *m*-nitrobenzoic acid at a pH below 1.6 and a precipitate that is useful (in the present context) only in the



pH range 1.8 to 2.6. At higher pH values the precipitate is a mixed one, probably of *m*-nitrobenzoate and hydrous oxide.

NOTES—

1. The saturated *m*-nitrobenzoic acid solution was prepared by dissolving 4 g of *m*-nitrobenzoic acid in 1 litre of hot water, allowing the solution to cool overnight, and then filtering off the acid that had crystallised out.

2. Perchloric acid was found to be a much more satisfactory solvent for the *m*-nitrobenzoate than nitric, hydrochloric or sulphuric acids.

3. The tartaric acid solution was added to complex the thorium so that the subsequent adjustment of the pH, in preparing the solution for polarography, would not cause its re-precipitation.

PROCEDURE—

The recommended procedure is that given in the preceding section, with the pH of precipitation controlled to  $2.15 \pm 0.10$  ( $\pm 0.20$  should, however, be permissible). This procedure yields a straight-line calibration curve for amounts of thorium up to at least 12 mg (see Fig. 3).

Results for the determination of thorium by this method in solutions containing greater concentrations of zinc and rare-earth elements and a much greater concentration of magnesium are summarised in Table I, but the initial volume was 25 ml and not 50 ml.

TABLE I

DETERMINATION OF THORIUM IN SOLUTIONS CONTAINING MAGNESIUM,  
ZINC AND RARE EARTHS

All solutions contained 230 mg of magnesium and 19 mg of zinc; the elements were present as chlorides in a volume of 25 ml

Amount of rare-earth elements present,* mg	Thorium taken, mg	Thorium found,† mg
12	$10.20 \pm 0.01$	$10.22 \pm 0.09$
22	$6.12 \pm 0.01$	$6.15 \pm 0.09$
49	$10.20 \pm 0.01$	$10.22 \pm 0.10$
74	$10.20 \pm 0.01$	$10.19 \pm 0.03$

\* Added in the form of a hydrochloric acid solution of mischmetal.

† The  $\pm$  value represents the over-all spread in the wave-height measurements of the 5 polarograms recorded for each solution.

COMPOSITION OF THORIUM *m*-NITROBENZOATE—

The composition of thorium *m*-nitrobenzoate was determined by precipitating a known amount of thorium with *m*-nitrobenzoic acid (by the procedure given above, the pH being  $2.15 \pm 0.10$ ), dissolving the washed precipitate with hot 4 *M* perchloric acid and determining the amount of *m*-nitrobenzoic acid polarographically. The linear calibration curve for these determinations was obtained from measurements with aliquot portions of a standard solution of *m*-nitrobenzoic acid, prepared from acid that had been recrystallised three times from hot water. Before the adjustment of the pH of the calibration solutions and the addition of the supporting electrolyte, tartaric acid and perchloric acid (in amounts equal to those used when thorium was present) were added. The results of these experiments are given in Table II.

TABLE II

COMPOSITION OF THORIUM *m*-NITROBENZOATE

Thorium taken, moles $\times 10^4$	<i>m</i> -Nitrobenzoic acid found, moles $\times 10^4$	Molar ratio
0.803	3.19	3.97
1.605	6.4(6)	4.02
2.410	9.5(9)	3.98
3.221	12.6(5)	3.94
4.015	15.9(1)	3.96
4.81	19.1	3.97
4.81	19.0	3.95
4.81	19.2	3.99

Average = 3.97

The precipitate is clearly the tetra-(*m*-nitrobenzoate). Other workers have found the same composition by other methods.<sup>10,30</sup>

If the precipitate is assumed to be the tetra compound, then the failure of the molar ratio (Table II) to be exactly four can be attributed to incompleteness of the precipitation of the thorium. The divergence suggests that the precipitation was short of completeness by 0.7 per cent. Rather satisfactory verification of this was obtained in gravimetric experiments in which the nitrobenzoate precipitate obtained from a known amount of thorium was ignited to the oxide; the recovery of thorium was 99.5 per cent.

#### DISCUSSION

The conditions under which thorium gives with either *m*-nitrophenylarsonic acid, *m*-nitrobenzoic acid or 8-hydroxyquinoline an analytically useful precipitate are not unduly restrictive. Each precipitate is readily soluble in an appropriate medium, and each of the organic reagents gives an easily measurable polarographic wave. For each there is a strictly linear relationship between the diffusion current of the reagent and its concentration, at least over a substantial range of concentrations.

Although the polarographic procedures for the determination of thorium with 8-hydroxyquinoline are very convenient, they are restricted in application, owing to the unselective character of 8-hydroxyquinoline as a precipitant.

The precipitation of thorium by *m*-nitrophenylarsonic acid is more attractive, because of the more selective precipitating ability of *m*-nitrophenylarsonic acid. The polarographic procedure that was developed by using this reagent is, however, rather lengthy, because of the 2-hour digestion period for the coagulation of the thorium *m*-nitrophenylarsonate. The use of heat to hasten coagulation is deemed unwise in view of the findings of VanDalen and Graham<sup>27</sup> in their work with titanium *m*-nitrophenylarsonate.

The method for thorium with *m*-nitrobenzoic acid combines the speed of the 8-hydroxyquinoline procedure and the selectivity of the *m*-nitrophenylarsonic acid procedure. The range of allowable pH values for the precipitation of thorium by *m*-nitrobenzoic acid is practicable, although admittedly it is narrow.

*m*-Nitrobenzoic acid is a very selective precipitant, being peculiarly adapted to the determination of quadrivalent elements (except titanium). Under appropriate conditions, thorium, zirconium and hafnium, and quadrivalent cerium and plutonium, can be quantitatively precipitated by this reagent. It does not, however, precipitate trivalent cerium<sup>11</sup> or plutonium.<sup>31</sup> Mercury in either state can be precipitated in a cold but not a hot solution, and stannous and stannic tin can interfere<sup>10,11</sup> (probably owing to hydrolysis effects). As mentioned earlier, *m*-nitrobenzoic acid has, with proper control of the pH of precipitation, been used to separate thorium and zirconium.

Crepaz and Marchesini<sup>32</sup> reported that barium, aluminium, lead, copper and lanthanum, amongst other elements, give precipitates with *m*-nitrobenzoic acid (introduced into the solution as the ammonium salt) at a pH of 3.3. We have found that these elements (and also trivalent rare-earth elements obtained from mischmetal) give no precipitates that contain nitrobenzoate over the pH range 2.1 to 8.0, when the elements are present in the initial solution at concentrations up to at least 40 mg per 50 ml of solution (four times the concentration of the thorium, in which we were interested). Neish<sup>10</sup> or Osborn<sup>11</sup> or both also found that *m*-nitrobenzoic acid does not precipitate these elements. Further evidence that trivalent lanthanide elements need not interfere in the determination of thorium by *m*-nitrobenzoic acid is furnished by the results in Table I.

Osborn<sup>11</sup> reported that *m*-nitrobenzoic acid quantitatively precipitates thorium from a solution that is 0.02 *N* in nitric acid; such a solution has a pH at the lower end of the range of pH that we found appropriate (pH 1.8 to 2.6). Crepaz and Marchesini,<sup>30</sup> in a study of the precipitation of thorium by *m*-nitrobenzoic acid in relation to the pH of the solution after precipitation, reported that no precipitate is formed when the pH is less than 1.9, that in the pH range 1.9 to 2.4 thorium is precipitated as the tetra-(*m*-nitrobenzoate), but not quantitatively, and that when the pH is above 2.4 thorium is precipitated quantitatively but not solely as the *m*-nitrobenzoate (the precipitate being a mixed one of indefinite composition).\*

\* Murthy *et al.*,<sup>19</sup> in a study of the use of *m*-nitrobenzoic acid for the separation of thorium from uranium, used a pH of 2.6 to 2.8 for the precipitation of thorium. Their method of analysis would not, however, distinguish between a thorium nitrobenzoate precipitate and hydrous thoria; their precipitate may well have been a mixed one. These workers reported that at pH values below 2.6 the precipitation of thorium by *m*-nitrobenzoic acid was "incomplete."

According to these workers, then, there is no pH range over which thorium can be quantitatively taken out of solution by *m*-nitrobenzoic acid in the form of a precipitate of constant composition. Our results confirm their finding that the *m*-nitrobenzoate of thorium is the tetra compound; that, at a pH of about 2.4—we would say 2.6—and above, the precipitate is not pure thorium tetra-(*m*-nitrobenzoate), the contaminant probably being hydrous thoria; but, by contrast, we precipitated thorium tetra-(*m*-nitrobenzoate), almost quantitatively (99.4 per cent.), at a pH somewhat below 1.9 (as did Osborn<sup>11</sup>) and, more particularly, precipitated a constant amount of the tetra-(*m*-nitrobenzoate) over a significant range of pH (Fig. 1).

Each of the curves in Fig. 1 has a straight-line portion that "breaks" at the same pH, 2.6. At this pH the hydroxyl-ion concentration of the solution has apparently become sufficiently high for hydrous thoria to begin to be precipitated.

The results in Table I indicate that the polarographic method with *m*-nitrobenzoic acid is applicable to the determination of thorium (when present at about the 3 per cent. level) in magnesium-base alloys containing zinc (about 6 per cent.) and rare-earth elements (up to about 21 per cent.). If zirconium should be present in the alloy, a prior separation from thorium would be required.

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## The Photometric Determination of Small Amounts of Silicon in Nickel and Nickel Alloys Used in Electronic Devices

By T. R. ANDREW

A procedure is described suitable for the photometric determination of silicon in nickel used in electronic devices and in nickel alloys containing up to 4 per cent. of tungsten. Silicon is determined photometrically at  $810\text{ m}\mu$  as the blue reduced molybdosilicate. A precision of  $\pm 0.001$  per cent. of silicon is claimed on a sample weighing  $0.25\text{ g}$  and the method can be applied to samples weighing only  $12.5\text{ mg}$ , such as may be available as single cathodes from electronic valves.

The use of phosphoric acid to retain tungsten in solution restricts the acidity range within which quantitative formation of molybdosilicate is achieved, but the permissible tolerance of acid concentration is sufficiently great to permit the method to be used for routine determinations.

NUMEROUS variants<sup>1,2,3</sup> of the molybdenum-blue method have been proposed for the determination of the silicon content of nickel used in electronic devices, but none of these procedures seemed suitable for the examination of nickel alloys containing less than 0.01 per cent. of silicon. In these laboratories, the ferrous sulphate - oxalic acid method of Gentry and Sherrington<sup>4</sup> has been used for a number of years and, with the appearance<sup>5</sup> of a modified version of this method, it was decided to study the procedure with a view to ascertaining its suitability for the determination of low concentrations of silicon.

In view of the use as cathode material of nickel containing additions of tungsten, it was obviously desirable to include such alloys in any study to be made. The major difficulty envisaged was the presence of tungsten, which was precipitated under the conditions of solution used. It has been claimed<sup>6,7</sup> that no silicon is lost on this precipitate, but, in view of the small amounts of silicon involved, it was thought preferable to have complete solution of the tungsten.

The use of oxalic, tartaric or citric acid to keep the tungsten in solution was not possible, since these acids prevent the formation of molybdosilicate. Although, with the hydrofluoric acid solution technique of Case,<sup>8</sup> the tungsten alloys were completely dissolved, a precipitate of tungstic acid formed when the fluoride was complexed with boric acid. Attention was therefore turned to the possibility of using phosphoric acid. It was found that within certain limits phosphoric acid could be used to give a clear solution in which silicon could be determined photometrically.

### EXPERIMENTAL

#### NICKEL AND TUNGSTEN-FREE NICKEL ALLOYS—

Previous work<sup>5</sup> on the analysis of steels had shown the desirability of investigating the relationship between the concentration of solvent acid and the formation of molybdosilicate. As only one solvent acid, nitric acid, is commonly used to dissolve nickel, this was a relatively simple matter. After it had been verified that the absorption curve of the molybdenum blue formed under the conditions of test was the same as that obtained from steels<sup>5</sup> and from pure solutions,<sup>9</sup> a graph was plotted in which the optical density of the molybdenum blue, after 15 minutes had been allowed for the formation of molybdosilicate, was related to the amount of nitric acid used. This is shown in Fig. 1, from which it is seen that, within a wide range (4 to 13 ml) of solvent-acid addition, reproducible recovery of silicon can be achieved. This range (pH 0.6 to 1.35) is very much wider than that reported in the analysis of steels, and it supports the suggestion<sup>4,9</sup> that the presence of iron exerts a marked influence on the formation of molybdosilicate under these conditions. Throughout the entire usable range of acid concentration, the colour intensity was at a maximum after the silicate - molybdate solutions had been set aside for less than 10 minutes.

A linear calibration curve was obtained by using the proposed method, with a blank value equivalent to 0.004 per cent. of silicon. No interference was experienced from 0.1%

of phosphorus, 5% of manganese, 5% of aluminium, 10% of barium, 10% of strontium, 10% of cobalt or 10% of molybdenum. These amounts were chosen to represent the limiting composition of possible alloys and do not necessarily indicate the maximum amounts that could have been tolerated.

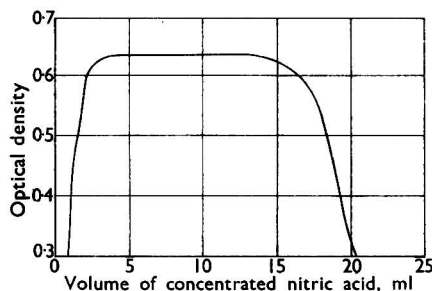


Fig. 1. Effect of concentration of solvent acid

One of the features of the method of Gentry and Sherrington<sup>4</sup> is the use of ferrous - ferric iron mixtures as reducing agents. This has been maintained in the present method and no fading has been experienced over periods up to 18 hours, although such fading has been reported<sup>10</sup> in the absence of ferric iron. The use of ferric - ferrous sulphate and oxalic acid as reagents, however, gives rise to a fairly high optical density in the compensating solution. It was not found possible to reduce this by replacing the oxalic acid by either tartaric or citric acid,<sup>11</sup> but it was possible to reduce the concentration of the ferrous ammonium sulphate - ferric ammonium sulphate solution used, provided that the ferrous to ferric ratio was maintained constant.

#### NICKEL AND NICKEL ALLOYS CONTAINING UP TO 4 PER CENT. OF TUNGSTEN—

Before proceeding to any critical evaluation of a method in which phosphoric acid was to be used, it was necessary to establish the amount of phosphoric acid required for solution of the tungsten present and to verify that the existing reagents were sufficient to deal with possible interference from molybdophosphate. A value of 4 per cent. of tungsten in nickel was taken as representing the probable upper limit of tungsten content of any alloys proposed for use as cathodes. Some 0.25-g portions of such an alloy were attacked with 16 ml of 8 N nitric acid to which various amounts of 1 per cent. phosphoric acid had been added. The resulting solutions were then examined visually, with the following results—

Volume of 1 per cent. phosphoric acid added, ml	0	0.1	0.5	1.0	2.0	3.0	5.0	10.0
Appearance of solution	..	..	..	..	..	..	..	..
				Containing precipitate		Turbid		Clear

From a consideration of these results it appeared that 5 ml of 1 per cent. phosphoric acid were sufficient to dissolve 4 per cent. tungsten - nickel alloys. This amount of phosphoric acid corresponded to 9 per cent. of phosphorus in the alloy and it was necessary to examine the effect of this large amount of phosphorus on the colour-forming reaction. Consideration of the dilution of the sample and of the aliquot finally taken indicated that the amount of phosphorus present in the final solution was not sufficient to interfere to any great extent with the ammonium molybdate concentration. It remained to decide whether the usual addition of oxalic acid would be sufficient to prevent reduction of the molybdophosphate formed. A few experiments served to confirm that, although molybdophosphate was formed, as shown by the development of a strong yellow coloration, it caused no interference with the silicon determination.

The tolerance of the method to acidity was determined as previously described, and the results are shown diagrammatically in Fig. 2, from which it is apparent that the addition of phosphoric acid had an influence on the permissible range of acid concentration, probably owing to, in part, disturbance of the balance of reagents. Nevertheless, a tolerably wide range of acidities (4 to 12 ml) was available, provided that the phosphoric acid addition was closely controlled. This should not present any difficulty in practice.

As it had been established that the method was possible, a study was made of the effect of additions of phosphoric acid less than that needed to keep the tungsten in solution and of allowing any tungstic acid formed to settle before taking an aliquot for colour formation. The results on a sample to which 0.1 per cent. of silicon had been added were as follows—

Volume of 1 per cent. phosphoric acid added, ml ..	1.0	2.0	3.0	4.0	5.0
Optical density (with that of the blank subtracted) ..	0.803	0.810	0.819	0.827	0.827
Appearance of solution ..	Turbid		Faint turbidity	Clear	

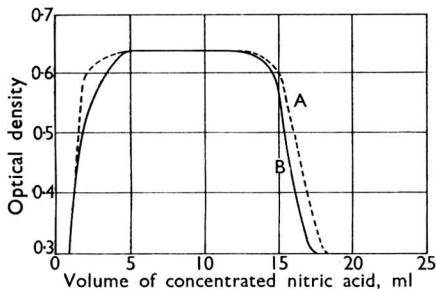


Fig. 2. Effect of concentration of solvent acid in the presence of phosphoric acid: curve A, 5.0 ml of 0.8 per cent. phosphoric acid; curve B, 5.0 ml of 1.0 per cent. phosphoric acid

These results confirmed that the addition of phosphoric acid to maintain a clear solution was beneficial and also showed that minor variations in the amount of phosphoric acid present, such as might be experienced during routine operation of the method, would not cause any alteration in the sensitivity of the method.

The rate of formation of molybdosilicate was studied for two concentrations of phosphoric acid at three points on their acidity curve (Fig. 2) and the results are shown in Fig. 3 (a) and (b). These curves show that at the lower acidities the maximum colour is rapidly developed, but that at the higher acidities a longer period of standing is required. Throughout this work a standing time of 20 minutes has been used, as being suited to batch operation.

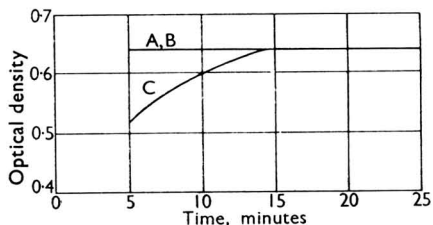


Fig. 3(a). Effect of time for formation of molybdosilicate in presence of 5.0 ml of 0.8 per cent. phosphoric acid: curve A, 4.0 ml of nitric acid used; curve B, 8.0 ml of nitric acid used; curve C, 12.0 ml of nitric acid used

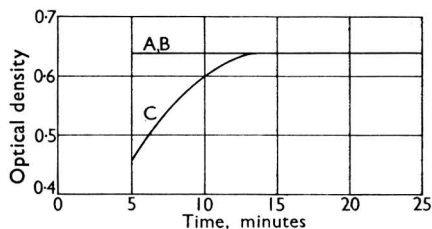


Fig. 3(b). Effect of time for formation of molybdosilicate in presence of 5.0 ml of 1.0 per cent. phosphoric acid: curve A, 4.0 ml of nitric acid used; curve B, 8.0 ml of nitric acid used; curve C, 12.0 ml of nitric acid used

The calibration curve obtained was linear and identical with that previously obtained for the determination of silicon in nickel.

During the development of this method, it was noticed at one point that occasional—apparently random—precipitation of ammonium molybdophosphate took place. It was not found possible to prevent this by chemical means and the elimination of this interference was finally achieved by the use of scratch-free beakers. If precipitation of molybdophosphate does occur in routine practice, it is necessary to reject the solution and to take a fresh aliquot of the main solution.

## METHOD

## REAGENTS—

*Nitric acid*, 8 N.

*Phosphoric acid*, 1 per cent.—Dilute 10 ml of orthophosphoric acid, sp.gr. 1.74, to 1 litre.

*Ammonium molybdate solution*, 2.5 per cent. w/v—This solution should be stored in polythene.

*Oxalic acid solution*, 4 per cent. w/v.

*Reducing solution*—Dissolve 1.5 g of ferrous ammonium sulphate and 0.5 g of ferric ammonium sulphate in water, add 1.0 ml of 18 N sulphuric acid and dilute to 100 ml.

## PROCEDURE—

Weigh 0.25 g of sample into a 250-ml beaker. Add  $16 \pm 4$  ml of 8 N nitric acid and, with tungsten-containing samples, 5.0 ml of 1 per cent. phosphoric acid. Warm to dissolve, add 100 ml of warm water and boil gently for 5 minutes. Cool and transfer to a 500-ml calibrated flask, dilute to the mark with water and mix.

Place by pipette 25-ml aliquots (A and B) in two clean dry unscratched beakers. To A, add from a pipette 10.0 ml of ammonium molybdate solution, mix, bring to  $25^\circ \pm 2^\circ$  C and set aside for 20 minutes. Then add, from pipettes in this order, mixing between additions, 10.0 ml of oxalic acid solution and 5.0 ml of reducing solution. To B add, from pipettes in this order, mixing between additions, 10.0 ml of oxalic acid solution, 5.0 ml of reducing solution and 10.0 ml of ammonium molybdate. Record the optical densities of these two solutions, using water as a comparison liquid. For preference a spectrophotometer should be used and the optical density determined at 810 m $\mu$  with a band width of about 4 m $\mu$ , but other conditions<sup>5</sup> may be employed if a spectrophotometer is not available.

## RESULTS

In order to determine the possible precision of the proposed method three samples were examined, one of which contained approximately 4 per cent. of tungsten. The results obtained on two samples of nickel that had been submitted as suitable for spectrographic standards are shown, together with the results on two tungsten-bearing samples, in Table I.

TABLE I

## REPRODUCIBILITY OF DETERMINATIONS OF SILICON IN NICKEL AND NICKEL ALLOYS

Sample .. .. .	A	B	C	D
Type of sample .. .. .	Nickel	Nickel	4% tungsten - nickel	4% tungsten - nickel
Certified value, % .. .. .	0.015	0.028	—	—
Number of analysts .. .. .	1	1	1	4
Number of determinations .. .. .	9	8	18	24
Mean, % of silicon .. .. .	0.0147	0.0294	0.0060	0.0075
Range, % of silicon .. .. .	0.0018	0.0027	0.0040	0.0029
Standard deviation, % of silicon .. .. .	$\pm 0.0003$	$\pm 0.0004$	$\pm 0.0003$	$\pm 0.0009$

It can be seen that within the range illustrated there is a 0.95 probability that a single determination is correct to within  $\pm 0.002$  per cent. of silicon. This precision is probably limited by the reagent blanks, which in the experiments described above were equivalent to a silicon content in the nickel of 0.002 to 0.005 per cent.

## CONCLUSIONS

The method that has been developed is suitable for the routine photometric determination of silicon at low (less than 0.1 per cent.) levels in nickel and nickel alloys. When a spectrophotometer and a 4-cm cell are used, the method covers the range of up to 0.1 per cent. of silicon in a 0.25-g sample. By taking a smaller sample weight, it may be extended above this range if due attention is paid to the control of the acidity. Again, although only a limited number is available and no critical examination of them has been made, it would also appear possible to take a larger sample weight to permit the more precise determination of silicon in alloys containing very small amounts.

The conditions are fairly flexible and the method is relatively rapid, although increased speed could be obtained at the expense of the wide tolerance at present permitted in respect

of the conditions of acidity. One condition that has been carefully controlled is the temperature of the solution during the formation of molybdosilicate. In our experiments this has been maintained at 25° C and any marked deviation from this value will affect the recorded rate of formation of the molybdosilicate.

For samples containing much more than 4 per cent. of tungsten it is expected that a fairly comprehensive re-evaluation of the method would be required, especially with regard to the balance of reagents.

Thanks are due to Mr. J. A. M. van Moll and the Directors of the Mullard Radio Valve Co. Ltd. for permission to publish this work and to Mr. R. J. Garwood for carrying out much of the experimental work.

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## The Determination of Sorbitol

By L. H. ADCOCK

Samples presented for determination of their sorbitol content often contain carbohydrates and the intramolecular ethers of sorbitol, usually referred to as the monoanhydrides of sorbitol. These interfere with the determination of sorbitol by oxidation with periodate. Separation of sorbitol from carbohydrates has been effected by degradation of the carbohydrates with alkali, followed by removal of the degradation products by means of ion-exchange resins; paper chromatography has been used for the separation of sorbitol from its anhydrides and other substances that react with periodate. Periodate procedures have been adapted to suit the various amounts of sorbitol separated by these methods, which range from 1 to 400  $\mu\text{g}$ . Examples are given of the application of these procedures to food samples, technical products and biological materials.

OWING to the increasing use of sorbitol, analytical methods are required for its determination in a variety of materials. It is being incorporated in a widening range of diabetic and other food preparations, and it is used as a constituent of humectants and in the manufacture of emulsifying agents. Sorbitol can readily be determined by its reaction with periodate, but samples of foods and technical chemicals presented for determination of their sorbitol content nearly always contain other substances that react with periodate, notably carbohydrates and the monoanhydrides of sorbitol. In technical chemicals both of these classes of substances may be present, but the presence of free anhydrides of sorbitol in foods is unlikely. Foods are more likely to contain fatty-acid esters of the anhydrides, which are used as emulsifying agents. Carbohydrates and the anhydrides of sorbitol may also be present in biological material, analysis of which may be required in the investigation of kidney function<sup>1</sup> and in the investigation of the metabolism of sorbitol<sup>2</sup> and its derivatives.

A satisfactory method for the separation of sorbitol from its anhydrides, before its determination by oxidation with periodate, is by chromatography, but, although various



methods have been suggested for the determination of sorbitol in samples containing carbohydrates, none of these is entirely satisfactory as a general procedure. Methods for its determination in mixtures with carbohydrates have either involved attempted removal of the carbohydrates with yeast,<sup>3</sup> which is without action on sorbitol, or have involved separate determination of the carbohydrates and then correction of the figure obtained on oxidation with periodate of the sorbitol-carbohydrate mixture.<sup>4</sup> The separation of sorbitol from the lower carbohydrates was not achieved by the earlier published solvent systems for chromatographic separation of the lower carbohydrates,<sup>5</sup> but solvent systems that do effect separation of sorbitol from certain of the lower carbohydrates have more recently been published.<sup>6</sup> Disadvantages of the yeast method are several. Although complete destruction by yeast of certain lower carbohydrates may be assumed, higher carbohydrates will need preliminary hydrolysis before attack by yeast is possible, and there may also be present or formed some carbohydrates that are not attacked at all by the yeast strain available. The washing of the yeast and the preparation of a suspension of known concentration add to the time and labour of the method. The method of separate determination of the carbohydrates presumes a knowledge of all the carbohydrates present, of methods for their determination and of their behaviour on oxidation with periodate. Although this method is satisfactory when only one pure known carbohydrate is present, even then it requires two separate analytical procedures to obtain the one sorbitol figure. The chromatographic method is more satisfactory than the other two, but it is not possible to be sure that a particular solvent system will separate sorbitol from all the carbohydrates present in an unknown mixture. For the utilisation of successful chromatographic separations of sorbitol, whether from carbohydrates, sorbitol anhydrides or from other substances that react with periodate, a technique is required for the determination of only a few micrograms of sorbitol.

A new method for the elimination of all carbohydrates from a sorbitol-carbohydrate mixture is now presented. It is based on the degradation of carbohydrates by alkali and does not require a knowledge of the carbohydrates present. A procedure for the determination by oxidation with periodate of 1 to 10  $\mu\text{g}$  of sorbitol from paper chromatograms is also presented. Examples are given of the applications of these methods to the determination of sorbitol in diabetic preserve and fruit squash, in biological samples and in technical sorbitol syrup.

#### OXIDATION OF SORBITOL WITH PERIODATE: CHOICE OF METHOD

The oxidation may be in acid solution, at 100° C or at room temperature, or in alkaline solution at room temperature. The oxidation in acid solution is usually followed by titration, with standard thiosulphate solution, of the iodine liberated on addition of potassium iodide to the excess of periodate and the iodate produced. The oxidation in alkaline solution is usually followed by a colorimetric determination of the formaldehyde produced. The titration method requires up to 400  $\mu\text{g}$  of sorbitol, preferably not less than 100  $\mu\text{g}$ , whereas the measurement of the formaldehyde may readily be carried out with 10 to 50  $\mu\text{g}$ . The measurement of the formaldehyde has been successfully scaled down for operation with 1 to 10  $\mu\text{g}$  of sorbitol from paper chromatograms. As not all substances oxidised with periodate produce formaldehyde, the measurement of the formaldehyde produced is more specific than the measurement of the periodate used.

#### OXIDATION WITH PERIODATE IN ACID SOLUTION: MEASUREMENT OF PERIODATE REDUCED BY 100 TO 400 $\mu\text{g}$ OF SORBITOL

*Conditions for the reaction*—It has been established that the ratio of moles of periodate reduced per mole of sorbitol oxidised can be kept constant at nearly the theoretical, 5 to 1, provided that an excess of periodate is maintained by the use of not less than 7.4 moles of periodate per mole of sorbitol. The oxidation appeared to be independent of the dilution of the solution, but the end-point of the starch-iodine titration was more difficult to detect in very dilute solutions.

*Apparatus*—The sorbitol figure obtained is the difference between two relatively large titration figures. Titration figures from not less than 20 ml to about 25 ml have to be determined to the nearest 0.02 ml or, preferably, 0.01 ml. This makes it necessary to deliver the first 20 ml separately, and the remainder from a microburette. It has proved accurate and convenient, especially for large groups of determinations, to add the 20 ml

from a bulb that has capillary tubing at the top and bottom and is calibrated to deliver about 20 ml between marks on the upper and lower capillary sections. The bulb may be attached to a reservoir, as shown in Fig. 1. The periodate - acid solution may be similarly delivered from a bulb having a capacity of 5 ml.

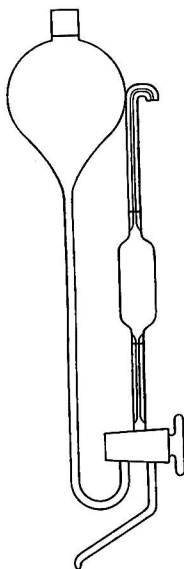


Fig. 1. Automatic pipette

#### METHOD FOR 100 TO 400 $\mu$ g OF SORBITOL

##### REAGENTS—

*Potassium periodate solution*—Dissolve 0.125 g of potassium periodate in water and dilute to 100 ml. Water distilled from potassium permanganate is recommended for this solution.

*Potassium periodate - sulphuric acid solution*—Mix 3 volumes of potassium periodate solution and 2 volumes of *N* sulphuric acid. Prepare freshly before use.

*Sorbitol solution*—Prepare a stock solution containing 400 mg per 100 ml, for dilution, as required, to a solution containing 20 mg per 100 ml.

*Sodium thiosulphate solution, 0.1 N*—For the preparation, as required, of 0.005 *N* solution.

*Potassium iodide.*

*Starch solution*—A solution containing 1 g per 100 ml.

##### PROCEDURE—

In 8-inch  $\times$  1-inch test-tubes place either 5 to 15 ml of water, with standard amounts of sorbitol, *e.g.*, 1 ml and 2 ml of the diluted sorbitol solution, or solutions for determination (100 to 400  $\mu$ g of sorbitol in not more than 25 ml, preferably 5 to 15 ml). Add to each tube 5 ml of potassium periodate - sulphuric acid solution. Whenever possible include tubes with duplicate portions of the solutions. Heat the tubes in a water bath at 100° C for 20 minutes. After cooling, to each tube in turn add potassium iodide and titrate with 0.005 *N* sodium thiosulphate, using starch solution as indicator. The differences between the titration figure for the water blank and the titration figures for the sorbitol solutions are a measure of the reduction of the periodate to iodate. The amount of sorbitol equivalent to 1 ml of 0.005 *N* sodium thiosulphate, theoretically 91  $\mu$ g, is calculated from the titration figures obtained for the oxidation of the standard amounts of sorbitol.

#### OXIDATION WITH PERIODATE IN ALKALINE SOLUTION: MEASUREMENT OF FORMALDEHYDE PRODUCED BY 10 TO 50 $\mu$ g OF SORBITOL

The two moles of formaldehyde produced by oxidation of 1 mole of sorbitol with periodate may be determined by the use of a chromotropic acid method such as that of Gibbons and

O'Dea.<sup>7</sup> In their method a periodate solution buffered with sodium bicarbonate is used, with removal of the excess of the reagents by lead dithionate, and MacFadyen's<sup>8</sup> conditions for development of the formaldehyde-chromotropic acid colour. The method described below is substantially their method, modified to obtain a more intense colour with formaldehyde and chromotropic acid from a given amount of sorbitol, and so to facilitate the determination of small amounts of sorbitol. In the preparation of lead dithionate (from barium dithionate, after treatment with sulphuric acid and neutralisation with lead carbonate), its precipitation from solution by acetone, rather than by ethanol as suggested by Gibbons and O'Dea, was found to give a more satisfactory material.

#### METHOD FOR 10 TO 50 $\mu$ g OF SORBITOL

##### REAGENTS—

*Sodium metaperiodate*—A 0.015 *M* solution in 0.045 *N* sulphuric acid.

*Sodium bicarbonate*—A freshly prepared saturated solution.

*Sodium metaperiodate - bicarbonate solution*—Mix 1 volume of sodium metaperiodate solution and 1 volume of sodium bicarbonate solution. Prepare freshly before use.

*Lead dithionate solution*—A solution containing 20 g per 100 ml; store it at 0° C.

*Sulphuric acid, diluted* (2 + 1).

*Chromotropic acid reagent solution*—Dissolve 0.5 g of the sodium salt of chromotropic acid in 50 ml of water, add 0.05 g of stannous chloride, and dilute to 250 ml with diluted sulphuric acid (2 + 1). Store the solution in the dark; it is stable for about 3 days only.

*Sorbitol solution*—Prepare a stock solution containing 300 mg per 100 ml, for dilution, as required, to a solution containing 15 mg per 100 ml.

##### PROCEDURE—

Evaporate to low bulk a volume of solution containing up to about 50  $\mu$ g of sorbitol, and finally evaporate it to dryness in a glass thimble or beaker on a steam-bath. Place standard amounts of sorbitol in similar vessels by evaporating in them 0, 1, 2 or 3 ml of dilute sorbitol solution. Add 1 ml of sodium metaperiodate - bicarbonate solution, ensure that all the material in the vessel is wetted, cover the vessel and leave it in the dark for not less than 1 hour. (Individual covers for the vessels are not essential. A set may be placed in a shallow tin and be both covered and kept dark by the lid of the tin.) Remove the bicarbonate and the excess of periodate by adding 1 ml of lead dithionate solution, mixing, and then spinning in a centrifuge in a stoppered tapered centrifuge tube. Without including any of the lead precipitate, by pipette transfer 1 ml of the supernatant solution into another centrifuge tube and add 9 ml of chromotropic acid reagent solution. Separate the lead sulphate by centrifugation and pour the clear solution into a stoppered tube, in which the formaldehyde-chromotropic acid colour is developed by heating in a water bath at 100° C for 30 minutes. All operations with chromotropic acid reagent solution must be shielded from bright light. Read the absorption of the coloured solutions in a spectrophotometer at 570  $m\mu$  or in an absorptiometer with Ilford No. 606 (yellow) filters, against the diluted sulphuric acid (2 + 1), since repeated exposure to the light affects the reagent blank solution. The use of calibrated bulbs having nominal capacities of 1 ml and 9 ml of the type previously described is recommended for delivery of the sodium metaperiodate - bicarbonate, lead dithionate and chromotropic acid reagent solutions.

#### OXIDATION WITH PERIODATE IN ALKALINE SOLUTION: MEASUREMENT OF THE FORMALDEHYDE PRODUCED BY 1 TO 10 $\mu$ g OF SORBITOL

Carry out the procedure described above, using one-tenth of the volumes of solutions prescribed. Do this by using Pasteur-type pipettes of nominal capacity 0.1 ml made from capillary tubing, and by the use of a bulb of the type already described, of nominal capacity 0.9 ml. The vessels for the oxidation step should have a pointed base to allow convenient collection of the solution in a Pasteur pipette, should have stoppers to prevent evaporation during the oxidation and should be wide at the top to facilitate evaporation of the sorbitol solution before oxidation. Use a micro 1-cm cell, of capacity 0.5 ml, in a Spekker absorptiometer for measurement of the formaldehyde - chromotropic acid colour.

#### TREATMENT OF CARBOHYDRATES

On being heated in alkaline solution under reflux, carbohydrates are converted to a complex mixture consisting largely of the alkali salts of lactic and saccharinic acids, whereas

sorbitol and its anhydrides are not attacked by alkali. Although sorbitol is unaffected by being heated under reflux in alkaline solution, it reacts with some of the substances produced from the carbohydrates. The extent of the reaction may be limited by using mild alkali and dilute solutions, and under these conditions it does not occur to such an extent as to cause low recovery figures for sorbitol, provided that the ratio of carbohydrate to sorbitol is not high. With a solution containing glucose and 40 mg of sorbitol per 100 ml, and sodium carbonate as the alkali, at not less than two equivalents for one mole of glucose, it has been shown that the recovery of sorbitol is 100 per cent. when the glucose to sorbitol ratio is 1 to 1, 95 per cent. when the ratio is 5 to 1 and 80 per cent. when the ratio is 20 to 1.

Ion-exchange resins separate the acids produced by the sugars from the sorbitol, which is then oxidised with periodate. Zeo-Karb 315 and De-Acidite FF were first used for separating the salts of the sugar acids from the sorbitol, but later the Zeo-Karb 315, which on being washed with water gave material that slightly interfered in the periodate - chromotropic acid procedure, was replaced by Zeo-Karb 225. Large volumes of pure distilled water have been kept over Zeo-Karb 225 and De-Acidite FF and the residues obtained on evaporation of the water did not react with periodate or interfere in the periodate - chromotropic acid procedure.

#### ION-EXCHANGE RESIN COLUMNS--

*Preparation and assembly of the column*—Prepare two U-tubes, each having one of its arms detachable by means of a B14 ground-glass joint close to the bend. The detachable arm is made from tubing of diameter 1 cm and is blocked by a coarse sintered-glass disc close to the B14 cone, which forms its lower end. The detachable arm of one of the U-tubes has a B14 socket at its upper end. The resin column is supported on the sintered-glass disc. The other arm of the U-tube is made from tubing that is less than 1 cm in diameter, and has an outlet arm above the level of the top of the resin column. The outlet arm is bent to be parallel with the arms of the U-tube. The outlet arm of one of the U-tubes has a B14 drip-end cone at its end, and the detachable arm used for this U-tube is the one without a B14 socket at the upper end (see Fig. 2). Fill each U-tube with sufficient water to cover the sintered-glass disc, and suck out any air bubble from beneath the disc. Air dry the ion-exchange resins. Use the Zeo-Karb 225 in bead form as supplied, and place 2 g in the U-tube that has a detachable arm with no B14 socket at the top. Grind the De-Acidite FF and use particles that are retained between 60 and 100-mesh sieves. Place 1 g of this resin in the second water-filled U-tube. Wash the column of Zeo-Karb 225 with 0.5 N sodium hydroxide and the column of De-Acidite FF with 0.5 N hydrochloric acid. Wash both columns with water. Regenerate them for use by passing a slight excess of 0.5 N hydrochloric acid through the Zeo-Karb 225 and a slight excess of 0.5 N sodium hydroxide through the De-Acidite FF. Wash each with distilled water until about 20 ml of washings require for neutralisation not more than one drop of 0.01 N alkali or acid, respectively, as shown by methyl red. (The water washing is quickly done by attaching the U-tube outlet to a water-pump, and covering the open end of the outlet side of the U-tube with the thumb or forefinger.) Then join the U-tubes, with the outlet of the U-tube containing Zeo-Karb 225 delivering into the U-tube containing De-Acidite FF.

*Use of the columns*—Place a small volume of sorbitol solution in the U-tube containing Zeo-Karb 225 and wash it through the resin columns with not less than 200 ml of distilled water delivered steadily to the columns over a period of several hours. This period may conveniently be made an overnight one. From columns as described, full recovery of 16 mg of pure sorbitol has been achieved with a wash volume of less than 200 ml. Larger wash volumes may be needed for full recovery of sorbitol from less simple solutions. Dilute the effluent from the columns to a known volume, or evaporate it to dryness, according to the amount of sorbitol present and according to the amount required by the periodate method selected for its determination.

Besides effecting the separation of sorbitol from acids produced by the sugars, the ion-exchange procedure also removes certain other materials, *e.g.*, amino acids and ascorbic, lactic, pyruvic and uric acids, which may be present in solutions of biological origin and are oxidised by periodate.

## CHROMATOGRAPHIC SEPARATION OF SORBITOL FROM ITS ANHYDRIDES—

The separation of sorbitol from its anhydrides is readily achieved by conventional paper-chromatographic procedures, with, for example, *n*-butanol saturated with water for development, and spray reagents based on those suggested by Cifonelli and Smith.<sup>9</sup> Details of a quantitative procedure are given on p. 433 for technical sorbitol syrup.

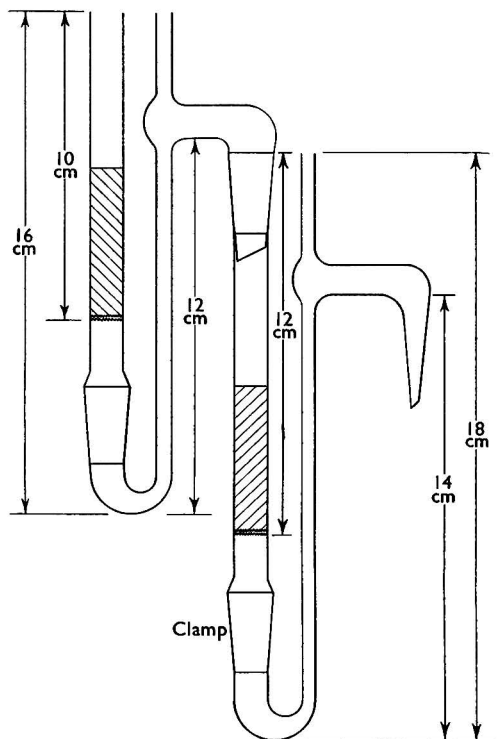


Fig. 2. Columns of ion-exchange resin

## APPLICATION OF THE METHODS

## DIABETIC PRESERVE—

*Procedure*—Disperse 200 g of preserve in warm water, cool the solution and dilute it to 1 litre. Dilute 20 ml to 500 ml. Filter a portion of this solution, and heat 2 ml of the filtered solution under reflux with 0.6 ml of *N* sodium carbonate solution and about 10 ml of water for 4 hours. Transfer the solution to ion-exchange columns as described above and wash through with 400 ml of distilled water. Dilute the effluent to 500 ml. Take 15-ml aliquots for oxidation with periodate in acid solution as described above.

*Results*—This method, applied to a preserve with a declared average sorbitol content of 58.7 g per 100 g of preserve, gave a figure of 59.8 g of sorbitol per 100 g of preserve. Recoveries of 10-mg portions of sorbitol, added at the stage of heating with alkali to triplicate determinations, which were completed with only 10-ml aliquots of the 500 ml of effluent from the resin columns, were 9.9, 9.8 and 10.1 mg.

## "SUGARLESS" FRUIT SQUASH—

*Procedure*—Dilute 10 ml of squash to 100 ml. Heat 1 ml under reflux with 0.6 ml of *N* sodium carbonate solution and about 10 ml of water for 4 hours. Then proceed as described for diabetic preserve, but use 10-ml aliquots for oxidation with periodate in acid solution.

*Results*—This method gave a figure of 16.3 g of sorbitol per 100 ml of squash for a sample of unspecified sorbitol content. Recoveries of 20-mg portions of sorbitol, added at the stage

of heating with alkali to triplicate determinations, which were completed with only 5-ml aliquots of the 500 ml of effluent from the resin columns, were 19.6, 19.6 and 20.1 mg.

#### BLOOD—

*Procedure*—Disperse 0.2 ml of blood in 3 ml of water and add 0.4 ml each of Somogyi zinc sulphate and barium hydroxide protein-precipitating solutions.<sup>10</sup> Shake well and spin in a centrifuge. Heat 1.6 ml of the supernatant solution under reflux with 0.6 ml of *N* sodium carbonate solution and about 10 ml of water for 4 hours. Transfer the solution to columns of ion-exchange resin as described previously, and wash through with 200 ml of distilled water. Evaporate the solution to low bulk by boiling, transfer it to a glass thimble or small beaker and complete the evaporation on a steam-bath. Oxidise the residue by the method described on p. 429 for 10 to 50  $\mu$ g of sorbitol. The sorbitol figure obtained must be corrected by the figure obtained by a simultaneous determination on a sample of sorbitol-free blood from the same source.

The standard amounts of sorbitol must pass through the protein precipitation step, since it causes a small loss of sorbitol. The loss appears to be independent of the amount of protein present. Standards suitable for storage and use as required may be prepared as follows. Mix 0, 5 and 10 volumes of sorbitol solution of concentration 30 mg per 100 ml with 80, 75 and 70 volumes of water, respectively, and add to each of these solutions 10 volumes of each of the Somogyi protein-precipitating solutions. Shake well and spin in a centrifuge. Seal portions of the supernatant solution in ampoules, and heat them in an autoclave at 7 lb per sq. inch for 30 minutes. Such solutions are stable for several months and may be used as standards for any determination for which the same batch of Somogyi solutions is used.

*Results*—When sorbitol was added to blood that had a sugar concentration of approximately 80 mg per 100 ml, in sufficient amount to produce a concentration of 80 mg of sorbitol per 100 ml, the sorbitol figures obtained by the given method were 78, 80 and 80 mg per 100 ml. When the sorbitol added gave a concentration of 15 mg of sorbitol per 100 ml, the figures obtained were 13, 13 and 14 mg per 100 ml.

#### URINE—

*Procedure*—Dilute 1 ml of urine with 5 ml of water, add 2 ml of each of the Somogyi protein-precipitating solutions and shake well. Spin in a centrifuge. Examine a suitable aliquot of the supernatant solution by the procedure described for protein-freed blood. The figure obtained from the determination of sorbitol-free but similar urine from the same subject must be applied as a correction.

*Results*—When sorbitol was added to urine to give a concentration of 60 mg of sorbitol per 100 ml, the method gave results of 60, 61 and 61 mg per 100 ml.

#### FAECES—

*Procedure*—Homogenise the sample in an Atomix. Stir 10 g of the sample with water, gradually increasing the amount of water until a uniform suspension is obtained of volume 125 ml. Dilute 25 ml of the suspension to 100 ml and shake a small portion with an equal volume of benzene to extract the fats. (The benzene should be purified by being shaken with potassium periodate and diluted sulphuric acid, and the mixture set aside for several hours with occasional shaking; the benzene is then separated and washed with alkali and water until it is free from periodate and is neutral.) Mix 2 ml of the extracted suspension of faeces with 4 ml of water and add 2 ml of each Somogyi protein-precipitating solution. Shake well and spin in a centrifuge. Take a suitable aliquot of the supernatant solution through the procedure detailed for protein-precipitated blood.

*Results*—When sufficient sorbitol was added to faeces to give 1.5 g and 3 g per 100 ml of faeces, the results obtained by this method were 1.4 and 2.9 g.

#### TECHNICAL SORBITOL SYRUP—

##### *Reagents*—

*Sorbitol solutions*—A series of solutions containing 0.25, 0.50, 0.75 and 1.0 g per 100 ml. *n*-Butanol, redistilled.

*Ethanol, aqueous*—Distil ethanol over sodium hydroxide and mix 1 volume of the distillate with 3 volumes of water.

*Potassium periodate*—A saturated aqueous solution.

*Benzidine solution*—Dissolve 1.84 g of benzidine in 50 ml of 90 per cent. ethanol and 20 ml of acetone.

*Hydrochloric acid*, 0.03 N.

*Hydrochloric acid - benzidine solution*—Mix 1 volume of 0.03 N hydrochloric acid with 1 volume of the benzidine solution freshly for use.

Whatman No. 1 paper for chromatography should be washed with water and dried in the air before use.

*Procedure*—Dilute the syrup to contain about 1 g of total solids per 100 ml. On paper that has been cut and marked suitably for descending-solvent chromatography, place equal volumes of diluted syrup solution and the standard sorbitol solutions by means of a micropipette of approximate capacity 1  $\mu$ l. (The micropipette may be a short length of capillary tubing prepared from narrow thick-walled glass tubing, the capillary being cut to a length found by trial to hold approximately 1  $\mu$ l when completely filled; the narrower end is ground to a point to facilitate delivery of the contents of the pipette; the pipette is set at an angle at the end of a glass rod so that it may be handled well away from the warmth of the fingers.) Flank the set of spots with marker spots of one of the standard sorbitol solutions. Condition the paper for 1 hour over *n*-butanol saturated with water and develop the chromatogram with that solvent for 16 hours. Allow the solvent to evaporate completely from the paper, cut off the marker-spot strips, and spray them with saturated aqueous potassium periodate solution. After 5 to 10 minutes, spray with the hydrochloric acid - benzidine solution, when sorbitol and other substances that react with periodate will show as white or yellow spots on a blue ground. (Approximate  $R_f$  values are as follows: sorbitol, 0.07; 1:5-sorbitol monoanhydride, 0.16; 1:4-sorbitol monoanhydride, 0.23; glycerol, 0.32; ethylene glycol, 0.51; propylene glycol, 0.67.) From the unsprayed portions of the chromatogram cut areas of similar shape and size corresponding to the sorbitol spots, standard and unknown. Elute the sorbitol from these areas of paper by suspending them at the end of condensers, over small flasks or tubes holding small equal volumes of the aqueous ethanol and heat the ethanol solutions for 1 hour under reflux. (Small sharp hooks suitable for the suspension of the papers may be formed from the tips of the condensers themselves, if the condensers are of the type fitted with "drip-end" standard ground-glass cones.) Treat the extracts as described on p. 430 for 1 to 10  $\mu$ g of sorbitol.

*Results*—The figures obtained by this method, for a syrup containing sorbitol, sorbitol monoanhydrides and sorbitol dianhydride in the ratio 1:2:5 by weight, with the sorbitol at 10 g per 100 g of syrup, were 9.7, 9.9, 10.0 and 10.2 g per 100 g of syrup.

I thank Messrs. Howards of Ilford Ltd. for permission to publish this work, and express my indebtedness to Professor C. H. Gray for assistance and facilities in the Department of Chemical Pathology, King's College Hospital Medical School, London, S.E.5.

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## The Analysis of Technical Chlorbenside and Fluorbenside

By D. J. HIGGONS AND W. H. STEPHENSON

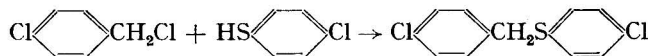
A method is presented for the determination of *p*-chlorobenzyl *p*-chlorophenyl sulphide in technical samples of the acaricide chlorbenside and *p*-chlorobenzyl *p*-fluorophenyl sulphide in the related fluorbenside, these compounds being the active constituents.

The method is based on the fact that oxidation of the isomeric sulphides in the materials gives a corresponding mixture of isomeric sulphones. After separation from by-products, this mixture is weighed and the proportion of the *p-p*-sulphone is obtained by reference to a eutectic melting-point curve. From this the amount of acaricidally active *p-p*-sulphide can be found. The total mixed isomeric sulphides may be also determined by oxidation to sulphoxide with bromine under controlled conditions.

Formulated products can be evaluated by the method after appropriate pre-treatment. A method is also outlined for the determination of a biologically undesirable impurity.

THE biological and chemical properties of chlorbenside (the accepted common name for *p*-chlorobenzyl *p*-chlorophenyl sulphide), an acaricide for the control of red spider, have been reviewed by Cranham, Higgons and Stevenson,<sup>1</sup> and colorimetric reactions for the compound, with particular reference to its determination in leaf-spray residues, have been developed by Higgons and Kilbey.<sup>2,3</sup>

Chlorbenside can be manufactured by the condensation of *p*-chlorobenzenethiol with *p*-chlorobenzyl chloride—



In the pure state it is a white crystalline solid of melting-point 74° C, which is stable in air. It is not easily reduced or hydrolysed, but it can be oxidised to the corresponding sulphoxide and sulphone.

Technical chlorbenside is a pale cream to fawn powder often having a characteristic odour. It contains 90 per cent. or more of the *p-p*-sulphide together with by-products, water and a trace of ash. Of the by-products, up to 5 per cent. of *o*-chlorobenzyl *p*-chlorophenyl sulphide may occur, *p*-chlorobenzaldehyde is present in amounts ranging from traces up to about 2 per cent. and bis-*p*-chlorophenyl disulphide, although usually absent, may be present up to 1 per cent.

Pure fluorbenside is a white crystalline solid of melting-point 36° C. It is much more volatile than the chloro compound, but its chemical properties are very similar. Technical fluorbenside is a white crystalline solid containing over 95 per cent. of *p*-chlorobenzyl *p*-fluorophenyl sulphide. It has an odour of ripe mushrooms. As it may be made in a similar manner to chlorbenside, the impurities are analogous, but are present in smaller amounts.

### EXPERIMENTAL

As these halogen-substituted aromatic sulphides were new substances, there was no information available about them in the literature. However, after a study of the literature on similar compounds various analytical methods were investigated.

(a) Fractional crystallisation was tried, as in the method of Cristol, Hayes and Haller<sup>4</sup> for DDT. This was unsatisfactory, as the presence of impurities such as *p*-chlorobenzaldehyde and bis-*p*-chlorophenyl disulphide increased the solubility of the chlorbenside in the solvents used.

(b) Condensation with chloramine T to form the sulphilimine<sup>1</sup> was attempted. Under all the conditions of reaction tried, condensation and oxidation proceeded simultaneously to give an irresolvable mixture of the sulphilimine and *p*-chlorobenzyl *p*-chlorophenyl sulphoxide as end-products.



(c) Ultra-violet and infra-red methods have both been studied, but up to the present it has not been possible to utilise these for analytical purposes.

(d) Oxidation with hydrogen peroxide was found to convert chlorbenside and *o*-chlorobenzyl *p*-chlorophenyl sulphide to the corresponding sulphones, which were insoluble in alkalis, whereas impurities such as *p*-chlorobenzaldehyde formed acidic compounds, which were soluble in alkalis. When the latter compounds were removed, an almost pure mixture of *p-p*- and *o-p*-sulphones was left. It was then possible from the weight of these sulphones to calculate the amount of "mixed isomeric sulphides" in the original sample. The melting-point of the mixed sulphones was determined and, by reference to a eutectic melting-point curve, the proportion of the *p-p*-sulphone in the mixture was found. From this figure the *p-p*-sulphide content of the original sample could be calculated.

TABLE I  
ANALYSIS OF ARTIFICIAL MIXTURES

Composition of mixtures									
<i>p-p</i> Chlor- benside, %	<i>o-p</i> Chlor- benside, %	Bis- <i>p</i> - chloro- phenyl di- sulphide, %	<i>p</i> -Chloro- benz- aldehyde, %	Dimer- capital,* %	Total sulphide ( <i>p-p</i> + <i>o-p</i> ), %	Deviation, %	<i>p-p</i> Isomer, %	Deviation, %	
100	0	0	0	0	97.9	-2.1	97.7	-2.3	
100	0	0	0	0	98.4	-1.6	98.4	-1.6	
89.7	10.3	0	0	0	98.0	-2.0	86.3	-3.4	
86.3	13.7	0	0	0	97.8	-2.2	82.4	-3.9	
79.8	20.2	0	0	0	97.7	-2.3	76.1	-3.7	
77.2	22.8	0	0	0	97.8	-2.2	76.4	-0.8	
94.5	0	5.5	0	0	92.9	-1.6	—	—	
90.0	0	10.0	0	0	88.4	-1.6	—	—	
0	0	100.0	0	0	0	0	—	—	
98.0	1	0.5	0	0.5	95.4	-3.6	93.3	-4.7	
98.0	1	0.5	0	0.5	95.2	-3.8	93.4	-4.6	
94.0	3	1.0	0.5	2.0	93.1	-3.9	89.9	-4.1	
94.0	3	1.0	0.5	2.0	93.4	-3.6	90.1	-3.9	
90.0	5	3.0	1.0	1.0	91.1	-3.9	86.4	-3.6	
90.0	5	3.0	1.0	1.0	91.9	-3.1	86.8	-3.2	
79.1	0	0	0	20.9	77.4	-1.7	74.7	-4.4	
65.7	0	0	0	34.3	64.4	-1.3	61.5	-4.2	
69.5	16.7	0	0	13.8	83.9	-2.3	65.3	-4.2	
54.6	6.5	0	0	38.9	59.1	-2.0	51.2	-3.4	
66.8	8.9	0	0	24.3	73.8	-1.9	63.1	-3.7	
68.4	31.6	0	0	0	97.9	-2.1	66.7	-1.7	

\* *p*-Chlorobenzaldehyde bis-*p*-chlorophenylmercaptal, which was regarded as a possible theoretical impurity, but was not found.

TABLE II  
REPLICATION OF ANALYSES

Batch No.	Total sulphides found, %	Standard deviation, %	<i>p</i> -Chlorobenzyl <i>p</i> -chlorophenyl sulphide found, %	Standard deviation, %
Chlorbenside—				
CT 19,016 ..	98.1, 98.7, 97.1, 97.3, 97.2, 97.0, 97.9, 98.8	} 0.6	97.2, 96.6, 96.2, 96.8, 96.2	} 0.4
CT 18,705 ..	92.7, 90.4, 89.8, 90.2, 89.7, 90.0		1.2	
Fluorbenside—				
CT 32,316 ..	97.6, 97.9, 96.7, 96.7, 97.8, 96.7, 96.9, 96.9	} 0.4	94.7*, 96.0*	—

\* Corresponding fluoro compound

Pure *p*-chlorobenzyl *p*-chlorophenyl sulphone melts at 150.4° C. Pure *o*-chlorobenzyl *p*-chlorophenyl sulphone melts at 120° C. The eutectic curve as determined by the thaw-melt

method of Rheinboldt<sup>5</sup> is shown in Fig. 1. The working range is shown in greater detail in Fig. 1 (a).

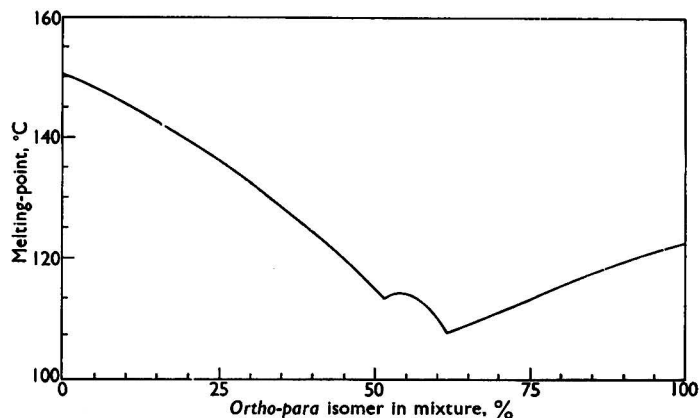


Fig. 1. Melting-point curve of mixtures of *p*-chlorobenzyl *p*-chlorophenyl sulphone and *o*-chlorobenzyl *p*-chlorophenyl sulphone

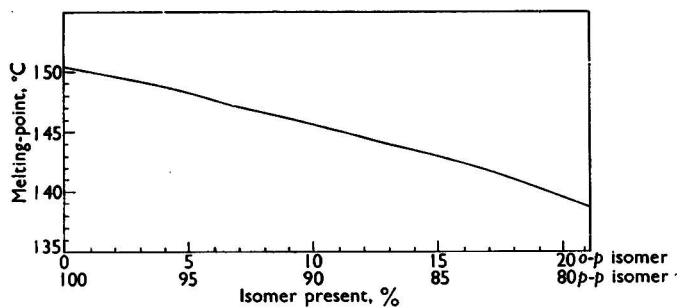


Fig. 1(a). Working range for chlorbenside

The melting-point of pure *p*-chlorobenzyl *p*-fluorophenyl sulphone is 147.7°C and of pure *o*-chlorobenzyl *p*-fluorophenyl sulphone 108.6°C. The eutectic curve is shown in Fig. 2 and the working range is shown in Fig. 2 (a). The determination of mixed isomeric sulphides gave lower results than the theoretical, as shown in Table I, which gives recoveries from a series of synthetic mixtures. This was shown to be due primarily to a slight solubility of the sulphones in the reagents and wash liquors. The correction factor that was derived from the examination of prepared mixtures resembling technical production material was +2.3 per cent. A similar correction factor must be used in the analysis of fluorbenside. Replication by the method is reasonable for an analysis of this nature (see Table II).

(e) Although chlorbenside in bulk is stable to atmospheric oxidation, it was realised that the gravimetric assay outlined above would not detect any sulfoxides or sulphones that might have been formed during manufacture, and in order to check this a bromimetric assay was developed.

Pure chlorbenside was quantitatively oxidised by bromine in glacial acetic acid to form the sulphoxide. This was in agreement with the report of Hamish and Tarbell<sup>6</sup> in their work on benzyl phenyl sulphide, but the somewhat complex system of immiscible solvents used by these authors was dispensed with, as the use of glacial acetic acid was found to be satisfactory for our purpose. As with most bromimetric assays, it was found that certain conditions had to be adhered to if reproducible results were to be expected. Of the variants studied, the temperature at which the oxidation was effected was found to be the

most important. Some results on a pure sample of chlorbenside by the method that was finally adopted, but at various temperatures, were as follows—

Temperature, °C	..	..	30	25	12.5				4
Mixed sulphides, %	..	..	102.0	101.9	100.0,	100.4,	101.0,	100.8	98.9

The assay procedure was conducted on pure samples of chlorbenside sulphoxide and chlorbenside sulphone, and these were shown to be non-reactive under the specified conditions.

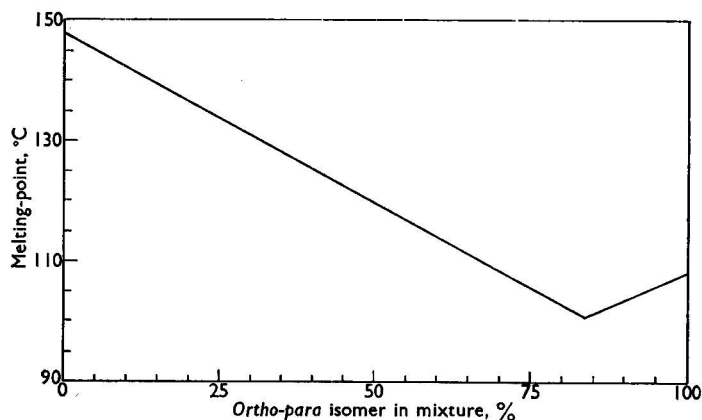


Fig. 2. Melting-point curve of mixtures of *p*-chlorobenzyl *p*-fluorophenyl sulphone and *o*-chlorobenzyl *p*-fluorophenyl sulphone

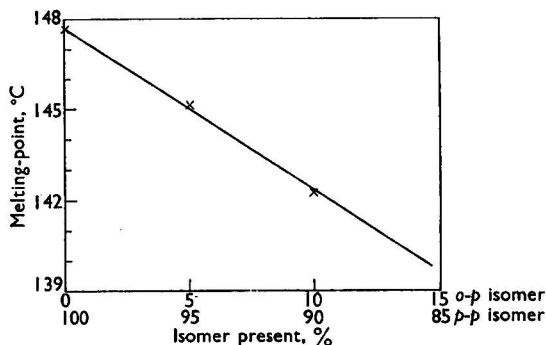


Fig. 2(a). Working range for fluorbenside

TABLE III

BROMIMETRIC ASSAY OF TECHNICAL AND RECRYSTALLISED CHLORBENSIDE AND FLORBENSIDE

Batch No.	Result (as total sulphides) for technical material, %	Result (as total sulphides) for batch recrystallised material, %
<i>Chlorbenside</i> —		
22,732	101.3	99.8
21,614	102.0	99.8
<i>Florbenside</i> —		
32,284	104.2	100.4
32,285	101.0	99.9

When the bromimetric assay was applied to pure chlorbenside with added amounts of impurities such as *p*-chlorobenzaldehyde and bis-*p*-chlorophenyl disulphide, the results were high. Similarly, all production material on being assayed was found to be slightly over 100 per cent. as mixed sulphides. This means that any significant amount of inert matter or oxidation product present would have the effect of bringing the "purity" level

as determined by this assay procedure to below 100 per cent. Results are shown in Table III and these together with values obtained by both the peroxide oxidation to mixed sulphones and the evaluation of the *p-p* isomer provide an assessment of the technical chlorbenseide.

(f) During the investigation it was established that small quantities of bis-*p*-chlorophenyl disulphide are sometimes present in chlorbenseide. From the biological standpoint large amounts of this compound are undesirable. The impurity is formed by the oxidation of the intermediate *p*-chlorobenzenethiol before its condensation and is not always wholly removed during the subsequent processes of purification of the chlorbenseide. A method for the evaluation of the amount of the impurity was therefore sought. The obvious procedure was by reduction of the disulphide linkage and the subsequent oxidative or argentimetric determination of the *p*-chlorobenzenethiol formed. Kolthoff, May, Morgan, Laitinen and O'Brien<sup>7</sup> have given details of the analysis of alkyl mercaptans for disulphide content by reduction of the disulphide to mercaptan with amalgamated zinc in acid - alcohol mixtures in a Jones reductor. After experimental work with the aryl disulphide, the use of a Jones reductor was abandoned, as it was found that the reduction proceeded quite satisfactorily in ordinary flasks. The amalgamated zinc/acid - alcohol mixture gave good reduction, but the treated zinc lost its activity if stored too long, and the temperature of reduction had to be kept as near 70° C as possible to ensure complete scission of the disulphide link. The effect of temperature on the reduction is shown in Table IV. Blank determinations were generally small.

TABLE IV

EFFECT OF TEMPERATURE ON RECOVERY OF BIS-*p*-CHLOROPHENYL DISULPHIDE

Conditions (1 hour's standing time)	Recovery, %
Room temperature, 22° to 24° C .. ..	64.7 70.3
Incubator at 37° C .. ..	87.6 87.0
Water bath at 50° C .. ..	96.7 97.2
Water bath at 70° C .. ..	99.3 99.8
On top of steam-bath at about 85° C .. ..	98.6 99.7
Blank on reagents (70° C) .. ..	0 0

METHOD FOR DETERMINING *p*-CHLOROBENZYL *p*-CHLOROPHENYL SULPHIDE IN TECHNICAL CHLORBENSIDE (AND *p*-CHLOROBENZYL *p*-FLUOROPHENYL SULPHIDE IN TECHNICAL FLUORBENSIDE)

## REAGENTS—

*Acetic acid, glacial.*

*Hydrogen peroxide, 100-volume.*

*Sodium hydroxide solution, 40 per cent. w/v.*

## PROCEDURE FOR MIXED SULPHIDE CONTENT—

Transfer about 0.5 g of the technical acaricide, accurately weighed, to a 250-ml stoppered flask. Add 10 ml of glacial acetic acid and warm on a hot-plate at about 100° C to dissolve. Add 2 ml of hydrogen peroxide, place the stopper in the flask loosely and put the flask on the hot-plate at about 100° C for 30 minutes. At the end of that time add a further 2 ml of hydrogen peroxide and again heat on the hot-plate for 30 minutes. Cool, dilute the mixture with 25 ml of water, shake gently and cautiously add sodium hydroxide solution until the mixture is alkaline. Swirl, and wash down the sides of the flask with sufficient water to produce a volume of about 100 ml. Insert the stopper, shake and set aside overnight. Filter through a Gooch crucible of porosity No. 3 and wash the precipitate with 300 to 400 ml of water or until the washings are no longer alkaline to litmus. Dry at 105° C to constant weight. Calculate the results by using the expressions—

Mixed sulphides in chlorbenseide, per cent.

$$= \frac{(\text{Weight of precipitate, g} \times 0.8936 \times 100)}{\text{Weight taken, g}} + \text{Correction factor,}$$

and similarly—

Mixed sulphides in fluorbenseide, per cent.

$$= \frac{(\text{Weight of precipitate, g} \times 0.8875 \times 100)}{\text{Weight taken, g}} + \text{Correction factor.}$$

The correction factor must be worked out under each condition of test. The values of 2.3 per cent. for chlorbenside and 0.5 per cent. for fluorbenside are those found to operate in these laboratories.

#### PROCEDURE FOR *p-p*-SULPHIDE CONTENT—

Determine simultaneously the melting-points of pure *p*-chlorobenzyl *p*-chlorophenyl sulphone,  $T$ , and of the sulphone obtained from the total isomeric-sulphide determination described above,  $T'$ , the temperature noted being that at which the last trace of solid disappears. Take the mean of three determinations. Determine the percentage of *p-p* isomer from the eutectic curve.

For between 90 and 100 per cent. of *p-p* isomer, each difference of 0.1° C in the two melting-points corresponds to 0.21 per cent. of *o-p* isomer in the sample.

For chlorbenside—

$$p-p \text{ Isomer, per cent.} = \text{Total isomeric sulphides, \%} \times \frac{[100 - 2.1(T - T')]}{100},$$

and for fluorbenside—

$$p-p \text{ Isomer, per cent.} = \text{Total isomeric sulphides, \%} \times \frac{[100 - 2.0(T - T')]}{100}.$$

#### METHOD FOR DETERMINING TOTAL ISOMERIC SULPHIDES

##### REAGENTS—

*Acetic acid, glacial.*

*Bromide - bromate, 0.1 N*—Dissolve 3 g of analytical-reagent grade potassium bromate and 15 g of potassium bromide in 500 ml of distilled water. The reagent should be kept in a dark amber-coloured glass-stoppered bottle.

*Potassium iodide solution, 10 per cent. w/v.*

*Sulphuric acid, 3 N.*

*Sodium thiosulphate solution, 0.1 N.*

*Starch solution.*

##### PROCEDURE—

Dissolve about 0.15 g of the sample, accurately weighed, in 30 ml of glacial acetic acid in an iodine flask and cool to between 10° and 15° C. Add 20 ml of 0.1 N bromide - bromate, swirl and insert the stopper. Seal with 5 ml of potassium iodide solution and cool to 10° C. At the same time carry out a blank determination without the chlorbenside. After 10 minutes allow the solution of potassium iodide used as a seal to enter the flask, and wash down with 10 ml of 3 N sulphuric acid. Titrate with 0.1 N sodium thiosulphate. Starch solution may be used as indicator.

Using the following expression, calculate the result—

$$\text{Mixed sulphides, per cent.} = \frac{0.1 \text{ N bromine absorbed, ml} \times 1.340}{\text{Weight of chlorbenside taken, g}}.$$

#### METHOD FOR DETERMINING BIS-*p*-CHLOROPHENYL DISULPHIDE (IN CHLORBENSIDE ONLY)

##### REAGENTS—

*Iodine solution, 0.05 N.*

*Ethanolic sulphuric acid, 0.02 N*—Add 3 ml of concentrated sulphuric acid to 360 ml of 90 per cent. ethanol.

*Zinc amalgam*—Transfer 100 g of zinc shot to a beaker and cover completely with 20 per cent. w/v hydrochloric acid for 1 minute. Drain off the acid and wash with water. Add to the moist shot 27 mg of powdered mercuric chloride and stir for 1 minute, distributing the mercury salt over the surface of the zinc. Wash well with water and dry by rinsing with ethanol and then ether. This must be freshly prepared.

##### PROCEDURE—

Transfer about 1 g of chlorbenside, accurately weighed, to a 150-ml conical flask. Add 25 ml of 0.2 N ethanolic sulphuric acid, 5 ml of glacial acetic acid and 5 g of zinc amalgam. Warm to 70° C on a hot-plate and maintain this temperature as evenly as possible ( $\pm 3^\circ$  C) for 1 hour. Cool until the bulk of the chlorbenside has crystallised out and filter through a

No. 3 sintered-glass crucible. Wash the flask and crucible with 90 per cent. ethanol and titrate the filtrate and washings with 0.05 *N* iodine to the first appearance of a pale yellow tint.

Calculate the result from the following expression—

Bis-*p*-chlorophenyl disulphide in chlorbenside, per cent.

$$= \frac{\text{Volume of 0.05 } N \text{ iodine absorbed, ml} \times 0.01436 \times 100}{\text{Weight taken, g} \times 2}$$

#### THE ANALYSIS OF FORMULATED PRODUCTS

It is impossible to give methods that are applicable to all formulations of chlorbenside, but the following methods have yielded satisfactory results in our hands when various diluents and additives have been used—

- (i) *Dispersable powder formulations*—Extract a known weight of the powder with a known volume of acetone, avoiding evaporation. Evaporate an aliquot of the filtered acetone extract and treat it with peroxide as described above.
- (ii) *Vaporising solution formulations*—Determine the total solids on a portion of the material by cautiously evaporating the solvent on a steam-bath and then drying it at 105° C. Treat the dried residue with peroxide as described above.
- (iii) *Miscible liquid formulations*—As for vaporising solution formulations.

#### RESULTS—

Recoveries from formulated products are shown in Table V.

TABLE V  
RECOVERY OF CHLORBENSIDE FROM FORMULATIONS

Formulation	Chlorbenside added (100% <i>p-p</i> isomer), mg	Chlorbenside recovered, mg	Recovery, %
Dispersible powder .. ..	20.1	19.4	96.5
	20.1	19.4	96.5
Miscible liquid .. ..	20.0	19.5	97.5
	20.0	19.5	97.5

#### DISCUSSION OF RESULTS

The validity of the procedures outlined above primarily depends on the results obtained from the analyses of synthetic mixtures, and it is clear that the results for both "mixed isomeric sulphide" and "*p-p*-sulphide" are low, the mean deviations being -2.3 and -3.4 per cent., respectively. The wider deviation for the determinations of the *p-p*-sulphide is to be expected owing to the inaccuracies that are always associated with eutectic melting-point methods.

The only impurities that have been identified in technical chlorbenside are *o*-chlorobenzyl *p*-chlorophenyl sulphide, bis-*p*-chlorophenyl disulphide and *p*-chlorobenzaldehyde, and the results of the analyses of synthetic mixtures containing these are given. Many of these mixtures bear no resemblance to the composition of technical chlorbenside, but are included for the sake of completeness. *p*-Chlorobenzaldehyde bis-*p*-chlorophenylmercaptal might have been expected as an impurity and it has been included in synthetic mixtures, although it has never, in fact, been detected.

The analysis of "mixed isomeric sulphides" and "*p-p*-sulphide" obtained by the gravimetric procedure give the main insight into the composition of technical chlorbenside, but they will not, of course, reveal the presence of any significant quantities of the two oxidation products of chlorbenside, *p*-chlorobenzyl *p*-chlorophenyl sulphoxide and sulphone, which might conceivably appear in technical material owing to reaction with oxidising agents. Both oxidation products are themselves active acaricides,<sup>1</sup> but they do not possess the penetrating and diffusing power on leaf surfaces of chlorbenside and their presence is therefore undesirable.

The determination of "mixed isomeric sulphide" by the bromimetric procedure will readily reveal the presence of any such oxidation products and, when all the assay results are assessed together, the composition of any batch of technical chlorbenside can be obtained.

Analytical methods for florbenside have been worked out by analogy with those existing for chlorbenside and a complete investigation of the application of all the methods to this

compound has not been undertaken. Sufficient results are available, however, to show that the methods put forward for the analysis of chlorbenside are suitable for the analysis of fluorbenside.

The method for the determination of bis-*p*-chlorophenyl disulphide has been included as the presence of large amounts of this compound is undesirable from the biological standpoint and a method for its detection is therefore necessary.

We are grateful to Mr. A. S. Beidas, Mr. H. Taylor and Mr. L. Ellison for sections of the practical work. We also acknowledge help and advice from Dr. H. A. Stevenson, who also supplied pure samples of the various by-products.

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October 4th, 1956

## Recommended Methods for the Analysis of Trade Effluents

PREPARED BY THE JOINT A.B.C.M. - S.A.C. COMMITTEE ON METHODS FOR THE ANALYSIS OF TRADE EFFLUENTS

### Methods for the Determination of Aluminium and Zinc

#### Aluminium

##### PRINCIPLE OF METHOD—

In this method,<sup>1</sup> after destruction of the organic matter, the aluminium at pH 4.4 produces a red to pink lake with ammonium aurintricarboxylate (aluminon) and is determined colorimetrically.

##### APPLICABILITY—

The method is generally applicable. Substances known not to interfere are: up to 100  $\mu\text{g}$  of ferric iron; up to 10  $\mu\text{g}$  of copper; up to 100  $\mu\text{g}$  of manganese; more than 1000  $\mu\text{g}$  of phosphorus pentoxide (as orthophosphate).

##### RANGE—

For aluminium contents up to 20  $\mu\text{g}$ .

##### REAGENTS—

*Hydrochloric acid, 5 N*—Redistil 250 ml of hydrochloric acid, sp.gr. 1.18, diluted with an equal volume of distilled water, in an all-glass distillation apparatus. Collect the distillate and standardise to 5 *N*. Store the solution in a stoppered borosilicate-glass bottle.

*Starch solution*—Mix 1 g of soluble starch with 5 ml of cold distilled water and then add 95 ml of boiling distilled water. Heat to boiling, then cool. Store in a glass bottle in the dark, and prepare freshly every 5 days. Filter before use through a fast filter-paper (Whatman No. 41).

*Thioglycollic acid, dilute*—Dilute 2 ml of 90 per cent. thioglycollic acid to 100 ml. Prepare freshly every 5 days.

*Acetic acid, glacial*—Redistil glacial acetic acid in an all-glass apparatus.

*Ammonium hydroxide, redistilled*—Measure 500 ml of ammonium hydroxide, sp.gr. 0.880, into the flask of an all-glass distillation apparatus. Using a small flame, distil off the ammonia and absorb it in 300 ml of distilled water in a flask surrounded by ice. Guard against the solution sucking back during the distillation. Ascertain the concentration of the purified ammonium hydroxide either by titration or by determining the density.

*Ammonium acetate solution*—Measure a volume of the redistilled acetic acid equivalent to 210 g of  $\text{CH}_3\text{COOH}$ , dilute it with 100 ml of distilled water and, with stirring, add a volume of the redistilled ammonium hydroxide equivalent to 49.5 g of  $\text{NH}_3$ . Dilute the solution to 1 litre.

*Standard aluminium solution A*—Dissolve 1.757 g of aluminium potassium sulphate,  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ , in distilled water containing 50 ml of 5 *N* hydrochloric acid and dilute to 1 litre with distilled water.

*Standard aluminium solution B*—Dilute 5 ml of solution A to 250 ml with distilled water.

1 ml  $\equiv$  2  $\mu\text{g}$  of aluminium.

*Aluminon, 0.2 per cent. w/v aqueous solution*—Dissolve 1 g of the salt (ammonium aurintricarboxylate) in about 400 ml of distilled water, filter, and then dilute to 500 ml.



Aluminon is known to vary in quality. If the purchased material does not give a satisfactory range of standards, suitable material may be prepared by the following method—

Add 4 g of sodium nitrite slowly in small portions, with vigorous stirring, to 44 ml of concentrated sulphuric acid, sp.gr. 1.84, in a 250-ml beaker, and cool to 10° C. Then add, over a period of 5 to 10 minutes, 12 g of salicylic acid, with stirring. Cool to 3° C in crushed ice and add drop by drop 3.5 ml of an approximately 37 per cent. solution of formaldehyde, with vigorous stirring, keeping the temperature below 5° C. Allow this to remain in the ice-bath for a further hour, stirring every 5 minutes, and then allow the reaction to proceed for 20 hours in the cooling-bath so adjusted that the temperature only rises by 1° to 2° C for the first 7 hours and then gradually attains room temperature (20° C) over the remainder of the period. Next, pour the mixture slowly into 2 litres of cold distilled water, with constant stirring, allow it to stand for 1 hour, and filter it through a Buchner funnel fitted with a close-textured paper. Wash the residue three times with cold distilled water and return it to the beaker. Add 1 litre of distilled water and 50 ml of hydrochloric acid, sp.gr. 1.18, and boil for 2 to 3 minutes. Allow the solid to settle for 10 minutes and wash it three times by decantation with distilled water. Crush and break up the black mass with a flattened glass rod, and twice more repeat the boiling with the same amounts of distilled water and hydrochloric acid, followed by filtration and washing. Finally, dissolve the residue in an excess of ammonium hydroxide and evaporate this solution to dryness on a steam-bath. Grind the dry product to a fine powder and transfer it to a glass-stoppered bottle.

*Iron indicator solution*—A solution containing 1 µg of ferric iron per ml. Dissolve 0.5 g of ferric chloride,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , in 100 ml of distilled water; dilute 1 ml of this solution to 1 litre.

#### PROCEDURE—

Measure into a 50-ml stoppered calibrated flask a suitable volume (not more than 25 ml) of the acid solution, prepared as described under "Destruction of Organic Matter,"\* and containing not more than 20 µg of aluminium. Add 1 ml of iron indicator solution and 2.0 ml of dilute thioglycollic acid; then add redistilled ammonium hydroxide until the colour just changes to violet. Add 2.0 ml of 5 N hydrochloric acid, 3.0 ml of starch solution and 5 ml of ammonium acetate solution, in that order; then dilute to about 45 ml. Add 3.0 ml of aluminon solution, dilute to the 50-ml mark and mix thoroughly. Immerse the flask without the stopper in boiling water for exactly 4 minutes. The flask should be supported in the water bath on a stand approximately  $\frac{1}{2}$  inch high to avoid any local overheating.

Carry out a blank procedure on all the reagents.

After heating, remove the flask from the boiling water and allow it to cool gradually to room temperature during 1 hour; then place it in a water bath maintained at a temperature of  $20^\circ \pm 0.5^\circ \text{C}$  for 30 minutes. Adjust the volume to 50 ml if necessary and complete the determination colorimetrically by one of the following methods.

*Instrumental method*—Measure the optical densities of the test and blank solutions in a spectrophotometer or in an absorptiometer, using a 4-cm cell or a 1-cm cell according to the depth of colour, and using a wavelength of 5200 Å in a spectrophotometer or a suitable green filter in an absorptiometer. Use distilled water in the comparison cell. Read the number of micrograms of aluminium equivalent to the observed optical densities of the test and blank solutions from a previously prepared calibration graph, and so obtain the net measure of aluminium in the sample.

Prepare the calibration graph as follows (NOTE: A new calibration graph should be prepared each time a fresh batch of solid aluminon is used)—

Measure appropriate amounts of standard aluminium solution B covering the range 0 to 20 µg into a series of 50-ml calibrated flasks and dilute each to about 25 ml. To each add 2.0 ml of 5 N hydrochloric acid, 2.0 ml of dilute thioglycollic acid, 3.0 ml of starch solution and 5 ml of ammonium acetate solution, in that order; then dilute to about 45 ml. Treat each in the same manner as the sample, beginning at "Add 3.0 ml of aluminon solution . . ." in the first paragraph of the Procedure. Measure the optical densities of the solutions, using distilled

\* See *Analyst*, 1956, **81**, 59, or *Reprint No. 1*.

water in the comparison cell. Construct a graph relating the optical densities to the number of micrograms of aluminium.

*Visual colour-comparison method*—Prepare a series of standards as described for the Instrumental Method. Compare the colours of the sample and standards either directly in the flasks or after transferring to 50-ml Nessler cylinders.

Express the result as milligrams of aluminium per litre of sample.

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### Zinc

Two methods are recommended, depending on the amount of zinc present in the sample.

#### ZINC CONTENTS GREATER THAN 5 mg PER LITRE

##### PRINCIPLE OF METHOD—

In this method,<sup>1</sup> after destruction of the organic matter, zinc (together with certain other heavy metals) is extracted at pH 4.5 with a solution of dithizone in chloroform. Zinc, together with bismuth and cadmium, is then extracted from the chloroform phase with dilute hydrochloric acid. After evaporation of the acid extract, the zinc in the residue is treated with potassium iodide in the presence of potassium ferricyanide. The iodine that is quantitatively liberated is then titrated with thiosulphate. This reaction is specific for zinc.

##### RANGE—

For zinc contents greater than 5 mg per litre of sample.

##### APPLICABILITY—

The method is generally applicable.

##### REAGENTS—

*Ammonium acetate solution*—Dissolve 386 g of ammonium acetate in distilled water and dilute to 1 litre.

*Dithizone solution in chloroform*—Dissolve, without heating, 0.15 g of diphenylthiocarbazon (dithizone) in 100 ml of chloroform in a separating funnel. Free the solution from copper as follows—

To the solution contained in the separating funnel add 100 ml of distilled water and 5 ml of ammonium hydroxide, sp.gr. 0.880, and shake the mixture vigorously. Discard the chloroform layer and wash the alkaline liquid with two 5-ml portions of chloroform. Add 200 ml of analytical-reagent grade chloroform and then hydrochloric acid until the aqueous layer is colourless on shaking. Run off the chloroform solution and store it in a brown-glass bottle.

*Hydrochloric acid, diluted (1 + 1).*

*Hydrochloric acid, dilute (1 + 10).*

*Acetic acid, glacial.*

*Potassium ferricyanide solution, 1 per cent. w/v*—This solution should be freshly prepared.

*Potassium iodide solution, 5 per cent. w/v*—This solution should be freshly prepared.

*Ammonium hydrogen fluoride.*

*Perchloric acid, 60 per cent. w/v.*

*Hydrogen peroxide, 30 per cent. w/v (100-volume).*

*Sodium thiosulphate solution, 0.1 N.*

*Sodium thiosulphate solution, 0.002 N*—Make an appropriate dilution of the 0.1 N solution with freshly boiled and cooled distilled water. This solution should be prepared freshly each day and stored in the dark.

*Starch indicator solution, 1 per cent. w/v.*

## PROCEDURE—

Transfer to a separating funnel a suitable volume (containing preferably 0.1 to 1.0 mg of zinc, but not exceeding 40 ml) of the acid solution, prepared as described under "Destruction of Organic Matter," and add 10 ml of the ammonium acetate solution.

Add 5 ml of dithizone solution and shake the mixture vigorously. Allow the layers to separate\* and transfer the chloroform extract to a second separating funnel, leaving the aqueous layer in the first funnel. Wash the chloroform extract by shaking it with a mixture of 6 ml of ammonium acetate solution, 3 ml of diluted hydrochloric acid (1 + 1) and 10 ml of distilled water. Allow the layers to separate, transfer the chloroform layer to a third separating funnel, and wash it with 20 ml of distilled water. Transfer the chloroform layer to a fourth separating funnel, leaving the wash waters in the second and third funnels.

Again extract the liquid remaining in the first funnel with another 5 ml of dithizone solution, and follow the same washing procedure, using the wash liquids left in the funnels from the treatment of the previous extract. If necessary, repeat the process until the zinc has been completely extracted from the liquid in the first funnel, as indicated by the colour of the dithizone solution remaining unchanged after shaking.

To the combined dithizone - chloroform extracts collected in the fourth separating funnel add 10 ml of dilute hydrochloric acid (1 + 10). After shaking, run the chloroform layer into another funnel and transfer the acid solution to a 60-ml or 100-ml borosilicate-glass beaker. Wash the funnel that contained the chloroform solution with about 10 ml of distilled water, adding the washing to the contents of the beaker. Re-extract the dithizone solution with another 10 ml of dilute hydrochloric acid (1 + 10) and again wash the funnel with 10 ml of distilled water, adding the acid extract and washings to the liquid in the beaker.

Evaporate the contents of the beaker to dryness. Add to the residue 5 drops of perchloric acid and 5 drops of hydrogen peroxide, and evaporate to dryness on a hot-plate. Repeat the treatment until all organic matter has been destroyed and a white residue remains. Wash down the sides of the beaker with distilled water and again evaporate to dryness.

To the residue add 0.1 ml of glacial acetic acid and a "speck" (about 0.01 g) of ammonium hydrogen fluoride, and then 2 ml of potassium iodide solution and 2 drops of starch indicator solution. If a blue colour appears after the addition of the starch, add 0.002 *N* sodium thiosulphate solution until the colour is just discharged. Add about 0.5 ml of potassium ferricyanide solution to the mixture, stirring it with a glass rod, and titrate with 0.002 *N* sodium thiosulphate solution. (If possible the titration should be carried out by artificial light, but this is not essential.) The blue starch - iodide complex may be adsorbed on the precipitated zinc ferrocyanide, and if this occurs the precipitate serves as an indicator.

Express the result as milligrams of zinc per litre of sample.

NOTE—The end-point is usually quite definite: the blue starch - iodide colour returns after a few minutes, but this should be ignored.

1 ml of 0.002 *N* sodium thiosulphate solution  $\equiv$  0.196 mg of zinc.

## ZINC CONTENTS UP TO 5 mg PER LITRE

The method of determination recommended by the Society<sup>2</sup> is known to give accurate results for very small amounts of zinc, but it is not recommended as a routine method for trade effluents because of its complexity.

## PRINCIPLE OF METHOD—

After destruction of the organic matter, copper is removed if necessary and zinc is separated from other metals by extraction with dithizone at pH 4.7. Excess of

\* If a reddish purple colour does not appear in the chloroform layer, there is too little zinc present for this method to be applied.

dithizone is removed with sodium sulphide and the zinc - dithizone complex in carbon tetrachloride is then measured colorimetrically.

RANGE—

For zinc contents up to 5 mg per litre of sample.

APPLICABILITY—

The method is generally applicable.

REAGENTS—

*Distilled water*—For preparing all the reagents, use distilled water that has been twice redistilled from glass. It is recommended that the distilled water be stored in polythene bottles.

*Hydrochloric acid, 1.0 N*

*Carbon tetrachloride, redistilled.*

*Dithizone stock solution*—Dissolve 0.05 g of diphenylthiocarbazone (dithizone) in 100 ml of redistilled carbon tetrachloride.

*Dithizone extraction solution*—Extract 10 ml of the dithizone stock solution with two 50-ml portions of dilute ammonium hydroxide (50 ml of distilled water containing 2 ml of 10 M ammonium hydroxide) and then reject the carbon tetrachloride layer. Filter the combined ammoniacal extracts if necessary. Acidify the extract with dilute hydrochloric acid (about 1 per cent.) and extract the precipitated dithizone with 100 ml of carbon tetrachloride. Wash the extract with two 10-ml portions of distilled water, and filter it through a dry filter-paper.

This solution should be freshly prepared.

*Sodium acetate - acetic acid buffer solution*—Dissolve 136 g of sodium acetate,  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , and 58 ml of glacial acetic acid in distilled water, and dilute to 500 ml. Extract this solution with small portions of a 0.05 per cent. w/v dithizone solution in carbon tetrachloride, shaking the mixture for about 2 minutes each time. Repeat the extraction until the final extract is pure green in colour. Filter the solution through cotton-wool to remove any carbon tetrachloride.

*Sodium thiosulphate solution, 25 per cent. w/v.*

*Sodium sulphide solution, 0.04 per cent. w/v*—Dissolve 4 g of analytical-reagent grade sodium sulphide,  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , in distilled water and dilute to 100 ml. Dilute 1 ml of this solution to 100 ml. This solution must be freshly prepared.

*Sodium sulphate, anhydrous.*

*Standard zinc solution*—Dissolve 0.4398 g of zinc sulphate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , in distilled water, dilute to 1 litre and mix well. Dilute 10 ml of this solution to 1 litre. This solution should be freshly prepared.

1 ml  $\equiv$  1  $\mu\text{g}$  of zinc.

PROCEDURE—

Determine the acidity of a 10-ml portion of the acid solution prepared as described under "Destruction of Organic Matter." Adjust the acidity of a suitable portion (containing not more than 5  $\mu\text{g}$  of zinc) of the acid solution to 0.1 N; note the volume of the adjusted solution.

Add 5.0 ml of dithizone extraction solution, shake the mixture for 2 minutes, and then allow the layers to separate. Observe the colour of the dithizone in the carbon tetrachloride layer; excess of dithizone is indicated by a green or brownish green colour. If the colour of the carbon tetrachloride layer is red, continue the addition of the dithizone extraction solution, 0.5 ml at a time, with shaking, as directed above, until an excess is present, as indicated by the appearance of a green tint. Allow the layers to separate and discard the dithizone layer containing the copper complex. Repeat this extraction with dithizone extraction solution twice more, discarding the dithizone layer each time.

To the aqueous solution remaining in the separating funnel add half its volume of the sodium acetate - acetic acid buffer solution, mix and then add 1.0 ml of sodium thiosulphate solution. Add 4.0 ml of dithizone extraction solution, measured from a burette, shake the mixture for 2 minutes and allow the layers to separate. Transfer

the lower layer to a second separating funnel, filtering it through a small plug of cotton-wool. Wash the aqueous layer with 1 ml of carbon tetrachloride and filter the carbon tetrachloride through the cotton-wool plug. Repeat the extraction procedure a second time, when the dithizone layer will be green if the zinc content does not exceed 5  $\mu\text{g}$  and if the dithizone extraction solution is of satisfactory concentration. (This can easily be checked by extracting a known amount of zinc with the dithizone solution.) Filter the second extract through the same cotton-wool plug into the second separating funnel. Wash the aqueous layer with 1 ml of carbon tetrachloride as before. Shake the combined dithizone-carbon tetrachloride extracts for 10 seconds with 10 ml of sodium sulphide solution to remove excess of dithizone. Allow the layers to separate and transfer the lower layer to a third separating funnel. Wash the aqueous layer in the second funnel with 1 ml of carbon tetrachloride and add this to the main solution. Extract the carbon tetrachloride solution with further 10-ml portions of sodium sulphide solution until the aqueous layer is no longer yellow. Shake the carbon tetrachloride layer with about 1 g of anhydrous sodium sulphate and filter it through a dry 9-cm filter-paper (Whatman No. 41) into a 25-ml calibrated flask. Wash the funnel and the filter-paper with a few millilitres of carbon tetrachloride, adding the washings to the solution in the flask, and dilute the solution to the mark with carbon tetrachloride.

Carry out a blank procedure on all the reagents used.

Measure the optical densities of the test and blank solutions in a spectrophotometer or in an absorptiometer, using a 1-cm cell and using a wavelength of 5320 Å in a spectrophotometer or a suitable green filter in an absorptiometer. Use carbon tetrachloride in the comparison cell. Read the number of micrograms of zinc equivalent to the observed optical densities of the test and blank solutions from a previously prepared calibration graph and so obtain the net measure of zinc in the sample.

Establish the calibration graph as follows—

Measure appropriate amounts of standard zinc solution covering the range 0 to 5  $\mu\text{g}$  of zinc into a series of separating funnels and add to each 1 ml of 1.0 *N* hydrochloric acid and dilute the solution to 10 ml. Add 5 ml of the sodium acetate-acetic acid buffer solution and 1.0 ml of sodium thiosulphate solution. Extract the zinc as for the test solution, beginning at "Add 4.0 ml of dithizone extraction solution, measured from a burette, . . ." in the third paragraph of "Procedure," taking care that the treatment with sodium sulphide solution is exactly the same as in the test, *i.e.*, as regards duration of shaking, etc. Measure the optical densities, using a 1-cm cell, and construct a graph relating the optical densities to the number of micrograms of zinc.

Express the result as milligrams of zinc per litre of sample.

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## Notes

### IDENTIFICATION OF AMYLOBARBITONE (AMYTAL) AND PENTOBARBITONE SODIUM (NEMBUTAL) IN MIXTURES

ALTHOUGH paper chromatography gives adequate resolution of most of the commonly used barbiturates,<sup>1 to 10</sup> mixtures of amylobarbitone (5-isoamyl-5-ethylbarbituric acid) and pentobarbitone sodium [monosodium derivative of 5-ethyl-5-(1-methylbutyl)barbituric acid] are not readily separated.

The identification of amylobarbitone and pentobarbitone sodium has now been facilitated by making use of the reaction of concentrated sulphuric acid with some barbiturates, as described by Maynert and Washburn.<sup>11</sup> Pentobarbitone sodium heated with concentrated sulphuric acid for 1 hour at 100° C is readily dealkylated to 5-ethylbarbituric acid in 65 per cent. yield, whereas amylobarbitone is unreactive under these conditions.

If the product obtained by heating pentobarbitone sodium with sulphuric acid for 1 hour is chromatographed, with the water-poor phase of the system *n*-butanol - *n*-pentanol - ammonia (1:1:1) as mobile phase, two spots are obtained on the chromatogram. The major spot,  $R_F$  0.11, corresponds to 5-ethylbarbituric acid, while the second faint spot,  $R_F$  0.26, has not been identified. The latter spot is also obtained if the heating with sulphuric acid has been carried out for 2 hours.

Mixtures of amylobarbitone and pentobarbitone sodium, after being heated with acid, give three spots on chromatograms, corresponding to amylobarbitone, 5-ethylbarbituric acid and the unidentified spot mentioned above. Hence an unknown substance, shown already by paper chromatography to be amylobarbitone, pentobarbitone sodium or a mixture of both, may be positively identified by treatment with sulphuric acid, followed by further chromatography. It has been possible to carry out this procedure on quantities as small as 0.1 mg and on mixtures containing as little as 10 per cent. of pentobarbitone sodium in amylobarbitone.

#### METHOD

Heat 1 mg of a mixture containing the two barbiturates with about 0.05 ml of concentrated sulphuric acid in the glass extraction cup, having a capacity about 2.5 ml, of a small liquid-liquid extraction apparatus of the upward-displacement type, at 100° C for 1 hour. Then dilute the reaction mixture with 0.5 ml of water and continuously extract with ether. Dry the extract by means of anhydrous sodium sulphate and evaporate to dryness; dissolve the residue in 0.5 ml of chloroform and use 25 to 50- $\mu$ l aliquots of this solution for chromatography. The spots on the chromatograms are best located by the ultra-violet light - fluorescent screen technique described by Grieg.<sup>3</sup>

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### THE ISOLATION OF CARBON AS BARIUM CARBONATE IN STUDIES WITH CARBON-14

THE apparatus and procedures described below were designed for certain recent metabolic studies<sup>1</sup> in which carbon-14 compounds were used, but they are suitable for general use.

Materials containing carbon were oxidised to carbon dioxide by use of a chromic acid mixture as described by Van Slyke,<sup>2</sup> the carbon dioxide was absorbed in sodium hydroxide and the carbonate produced was precipitated as barium carbonate. Apparatus for these three steps is shown in Figs. 1, 2 and 3.

#### METHOD

##### APPARATUS—

*Combustion apparatus* (Fig. 1)—The central piece, A, is a short length of tubing with a B24 drip-end cone at the bottom, a B24 socket at the top and with B10 sockets attached as short branches on opposite sides of the tube to each other. The branches are midway up the tube and point upwards at about 45°. A calcium chloride tube, B, is at the top of the column, C, which is filled with soda lime, or preferably a self-indicating variety such as Indicarb, and has a B24 cone at its lower end, which rests in the B24 socket of A. Just below this socket it is lightly plugged with glass-wool, tapered, and continued as glass tubing of sufficient length to reach about halfway down the 100-ml conical flask, D, which is joined by a B24 socket to the lower end of A. In one of the branches of A is a tap funnel, E, and in the other a tube, F, which is filled with disodium hydrogen phosphate crystals to trap sulphuric acid and has a B10 socket at its end. The combustion apparatus is joined at F to the absorption apparatus by two short pieces of glass

tubing, each having a B10 cone at one end, these pieces being inserted in pressure-tubing almost to touch each other. The slight play allowed by the rubber promotes safe manipulation of the whole apparatus. All joints of the combustion apparatus, up to but not including the B10 cone that enters the absorption apparatus, are lubricated with syrupy phosphoric acid. The B10 cone is lubricated with silicone grease.

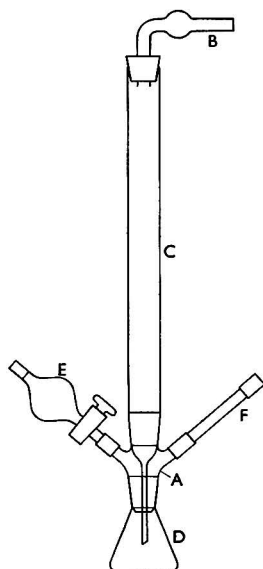


Fig. 1

Fig. 1. Apparatus for combustion

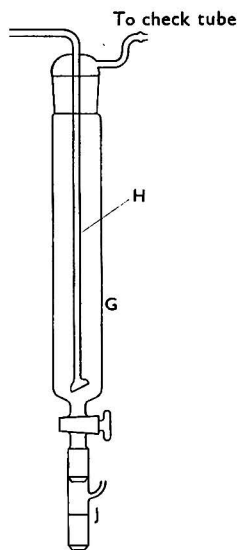


Fig. 2

Fig. 2. Apparatus for absorption of carbon dioxide

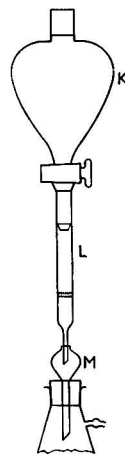


Fig. 3

Fig. 3. Apparatus for precipitation and collection of barium carbonate

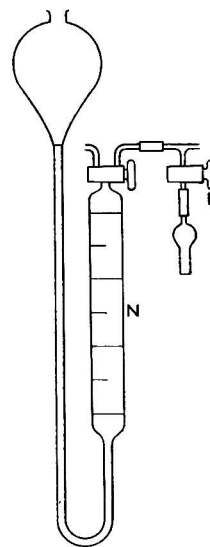


Fig. 4

Fig. 4. Apparatus for determining carbon dioxide in expired-breath samples

*Apparatus for absorption of carbon dioxide* (Fig. 2)—This apparatus is based on that proposed by Berlin, Tolbert and Lawrence<sup>3</sup> and subsequently modified by J. J. Scott (personal communication). The outer tube, G, is 30 cm long and 5 cm in diameter, with a B34 socket at the top and a stopcock, with B19 cone attached, at the bottom. A sintered-glass disc of porosity No. 3 and diameter 2 cm is set at an angle at the end of the inner tube, H, close to the bottom of the outer tube. The top of the inner tube is sealed through the domed B34 stopper of the outer tube. The inlet to the inner tube is a B10 socket. The outlet from the outer tube is through the B34 stopper. It leads to a small check tube, which allows observation of the rate of flow of air through the apparatus, and, if filled with barium hydroxide solution instead of water, provides a check on the absorption of carbon dioxide. A short piece of tubing with a side-arm, J, having a B19 socket at one end and a B19 cone at the other, is placed under the absorption tube so that the contents of the absorption tube may be transferred under vacuum to the tap funnel, K, of the precipitation apparatus.

*Apparatus for the precipitation and collection of barium carbonate* (Fig. 3)—This consists of a tap funnel, K, having a capacity of 250 ml and carrying B19 joints; of a filter tube, L, which can be weighed and has a B19 socket at the top, a sintered-glass disc of porosity No. 3 midway along it and a B14 cone on its tapered lower end; and of a Buchner flask, of capacity 500 ml, with an adaptor, M, with a B14 socket. With the exception of the stopcocks, all joints in the absorption apparatus and the precipitation and collection apparatus are kept unlubricated.

#### REAGENTS—

*Oxidising solution*—Mix 120 g of chromium trioxide, 330 ml of 85 per cent. w/w phosphoric acid and 90 ml of concentrated sulphuric acid. Slowly add 670 ml of fuming sulphuric acid (containing 20 per cent. of free sulphur trioxide). Then heat the mixture to 140° C.

*Potassium iodate*—Analytical-reagent grade, finely powdered.

*Sodium hydroxide solution*—A *N* solution containing 800 mg of hydrazine hydrochloride per litre. This solution must be free from carbonate and can be prepared by dilution of a concentrated solution, e.g., 32 to 33 ml of the clear supernatant solution from 1 part of sodium hydroxide in 1 part of water, by weight, diluted to 500 ml with water free from carbon dioxide.

*Barium chloride solution*—A solution containing 27 g per litre.

#### PROCEDURE—

Fill tube F (freshly for each combustion), and join the combustion and absorption sections of the apparatus. Place in the flask, D, a quantity of material for combustion containing not more than 24 mg of carbon. Wet material must be dried. Add about 3 g of potassium iodate, lubricate the joint, and clamp the flask in place. Place 30 ml of oxidising solution in the tap funnel, E. Place 200 ml of sodium hydroxide solution in the absorption tube, G, with the tube lowered sufficiently to keep the sintered-glass disc out of the solution. Connect the apparatus to a vacuum line, hold the tap funnel, K, in place on the adaptor below the tube G, and raise K, J and G together to seal the B34 joint of G with that of H, the inner tube of the absorption apparatus. Adjust the vacuum line to give a suitable flow rate, about 2 to 3 bubbles per second in the check tube. Run the oxidising solution into the flask, D, and heat it to maintain a small head of bubbles for 5 minutes. Continue to draw the stream of air through for a further 10 minutes with no further heating. Then turn the tap of G, slowly. (Fast turning causes the liquid in the check tube to suck into G.) When all the solution in G has emptied into K, disconnect the vacuum line. Open the absorption apparatus at the B34 joint that connects G and H, and wash down the sides of G and H with water free from carbon dioxide. Reconnect G and H, separate the absorption apparatus from the combustion apparatus, and pass water free from carbon dioxide from a squeeze-type wash bottle into the inside of H. Connect to the vacuum line to suck the washings into K. Again disconnect the vacuum line, open the apparatus as before, and repeat the washing of the sides of G and H. Remove K, insert a stopper, and mix the wash water with the main solution by swirling. (If the wash water is not mixed in, it later dilutes the added barium chloride solution before it reaches the main solution, and the form of the barium carbonate precipitate obtained is less suitable.) Add 20 ml of barium chloride solution. After not less than 15 minutes, place K, with a guard tube to absorb carbon dioxide instead of a stopper, in place on the weighed tube L. Allow a few millilitres of solution to run into the tube before completely sealing the joint between K and L. Filter the contents of K under vacuum, with the stopcock of K always fully open, never allowing L to become dry. When K is empty, remove the guard tube, rapidly wash the sides with water free from carbon dioxide, replace the guard tube and continue the filtration. After a second wash no guard is necessary and K may be separated from L, for final clearance of any barium carbonate adhering to K by means of a suitably curved rubber-tipped glass rod. Wash the barium carbonate in L until the washings give no reaction with neutral silver nitrate solution. Dry L at 110° C to constant weight.

TABLE I  
RECOVERY OF GLUCOSE, SORBITOL, URINE AND BLOOD AND OF VARIOUS  
ADDED MATERIALS

Material analysed	Amount taken	Added material	Amount of added material, mg	Theoretical equivalent of barium carbonate, mg	Barium carbonate recovered, mg	Recovery, %	Recovery of added material, %
Glucose	59.92 mg	—	—	393.5	389.0	98.9	—
	29.96 mg	—	—	196.8	197.9	100.6	—
	59.95 mg	—	—	393.7	398.7	101.3	—
Sorbitol	36.9 mg	—	—	239.6	235.9	98.4	—
	36.9 mg	—	—	239.6	238.8	99.6	—
	36.9 mg	—	—	239.6	237.3	99.0	—
Urine	1 ml	—	—	—	99.2	—	—
	1 ml	—	—	—	97.9	—	—
	1 ml	glucose	29.8	195.7	293.3	—	99.2 to 99.8
	1 ml	succinic acid	29.9	199.8	296.4	—	98.7 to 99.3
	1 ml	potassium hydrogen phthalate	25.6	197.8	299.0	—	101.0 to 101.7
Blood	0.20 ml	—	—	—	297.3	—	—
	0.20 ml	glucose	41.8	274.5	571.2	—	99.8



## RESULTS

Results for glucose, sorbitol, urine and blood and the recoveries of materials added to blood and urine are shown in Table I. Results for a sample of homogenised faeces are shown in Table II.

TABLE II  
RECOVERY OF HOMOGENISED FAECES AND OF ADDED GLUCOSE

Weight of sample, mg	Dry weight, mg	Added material	Weight of added material, mg	Theoretical equivalent of barium carbonate, mg	Barium carbonate recovered, mg	Barium carbonate recovery, mg per 1 g of faeces solids	Recovery of added material, %
600.5	106.8	—	—	—	852.5	7.98	—
493.7	86.1	—	—	—	694.6	8.07	—
494.0	85.7	glucose	30	197	857.9	—	96.8 to 97.4

## DETERMINATION OF CARBON DIOXIDE IN SAMPLES OF EXPIRED AIR

The apparatus shown in Figs. 2 and 3 may be used with that shown in Fig. 4 for the recovery of carbon from samples of expired breath. The apparatus shown in Fig. 4 is a calibrated tube, N, of capacity about 300 ml, attached at its lower end to a mercury reservoir, and having a two-way stopcock at the top. This stopcock is connected on the one side to the breath sample, *e.g.*, in a Douglas bag, and on the other side to a T-piece. One arm of the T-piece is connected by pressure-tubing and a B10 cone to the B10 socket of H of the absorption apparatus. The other arm of the T-piece leads to the atmosphere via a stopcock, P, and a soda-lime tube.

## PROCEDURE—

Fill N with mercury to the upper calibration mark. With stopcock P slightly open, place 200 ml of sodium hydroxide solution in G, connect the apparatus to a vacuum line, and, as previously described, raise K, J and G to close with H. Lower the mercury reservoir and draw a portion of the breath sample into N, to fill it to the lower calibration mark, at atmospheric pressure; seal N, raise the reservoir, connect N to the rest of the apparatus and close P. Repeat the sequence of operations beginning with "lower the mercury reservoir" as necessary until a sufficient quantity of carbon dioxide has been passed into G. Correct the total volume passed in these operations by the volume of the tube connecting the breath-sample holder and tube N.

I thank Howards of Ilford Limited for permission to publish this work.

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1. Adcock, L. H., and Gray, C. H., *Nature*, 1956, **177**, 329.
2. Van Slyke, D. D., *Anal. Chem.*, 1954, **26**, 1706.
3. Berlin, N. I., Tolbert, B. M., and Lawrence, J. H., *J. Clin. Invest.*, 1951, **30**, 73.

HOWARDS OF ILFORD LIMITED  
ILFORD  
ESSEX

L. H. ADCOCK  
December 19th, 1956

## THE DETECTION OF IODINE-CONTAINING COMPOUNDS ON PAPER CHROMATOGRAMS

THE use of the ceric sulphate - arsenious acid reaction for the detection of minute quantities of iodine-containing compounds has been described by Bowden, Maclagan and Wilkinson.<sup>1</sup> In their paper-chromatographic procedure the iodine-containing substances appear as white spots on a yellow background and the colour remains stable for 1 to 2 days.

In applying this method, it has been found that the life of the chromatograms can be extended by spraying them with a 1 per cent. aqueous solution of brucine sulphate. This causes the yellow background to become crimson, while the iodine-containing areas remain white. The darker background colour not only facilitates the interpretation of the chromatogram by producing greater contrast, but it also extends the life of the chromatogram to at least 1 month. The crimson colour results from the reaction of the excess of ceric sulphate with the brucine sulphate,<sup>2</sup> which inhibits any further reaction between the ceric sulphate and arsenious acid.

An alternative procedure involves the use of a 1 per cent. aqueous solution of sulphanic acid. The sulphanic acid combines with the ceric sulphate,<sup>3</sup> in a similar manner, to produce white spots with a brown background.

This work was supported by a grant from the Welch Foundation.

#### REFERENCES

1. Bowden, C. H., Maclagan, N. F., and Wilkinson, J. H., *Biochem. J.*, 1955, **59**, 93.
2. Sandell, E. B., "Colorimetric Determination of Traces of Metals," Second Edition, Interscience Publishers Inc., New York, 1950.
3. Montignie, E., *Bull. Soc. Chim. France*, 1939, **6**, 889.

BIOCHEMICAL INSTITUTE  
UNIVERSITY OF TEXAS  
AUSTIN, TEXAS

A. M. GAWIENOWSKI  
February 15th, 1957

#### THE DETERMINATION OF LEAD IN ORGANIC MATERIAL

In a previously described method,<sup>1</sup> lead is extracted from a solution of ashed organic material as the diethyldithiocarbamate complex. The solvent recommended for this extraction is a mixture of equal volumes of "sulphur-free" toluene and pentanol; recent experience has shown that some batches of toluene, even if stated to be "sulphur-free," can give rise to poor recoveries of lead when used in this method. This error can be avoided by treating the toluene - pentanol mixture with bromine; sufficient bromine should be added to produce a deep yellow colour, and after 30 minutes, the solvent is decolorised by shaking it with bisulphite solution and then washed with water.

In order to obtain complete conversion of lead to the diethyldithiocarbamate complex, it is necessary to allow the reaction to proceed for 15 minutes. In the method described, the citrate - bicarbonate solution should not be extracted with the solvent until 15 minutes after the addition of solid sodium diethyldithiocarbamate, and a similar period should be allowed between the addition of this reagent to the test solution, and extraction with the purified toluene - pentanol mixture.

#### REFERENCE

1. Gage, J. C., *Analyst*, 1955, **80**, 789.

IMPERIAL CHEMICAL INDUSTRIES LIMITED  
INDUSTRIAL HYGIENE RESEARCH LABORATORIES  
THE FRYTHE, WELWYN, HERTS.

J. C. GAGE  
March 27th, 1957

#### THE COLORIMETRIC DETERMINATION OF PHOSPHORUS IN STEEL AND COPPER-BASE ALLOYS

In a paper with the above title,<sup>1</sup> a colorimetric procedure for the determination of phosphorus based on the formation of phosphovanadomolybdic acid was described.

The experimental section contains reference to interference by arsenic and tables of results show that the presence of this element accounts for a positive error equivalent to about one-hundredth of its weight of phosphorus, *i.e.*, the presence of 0.05 per cent. of arsenic would introduce a positive error equivalent to about 0.0005 per cent. of phosphorus.

At the time of publication we were satisfied that the error due to arsenic was not greater than that indicated, but difficulty has since been experienced in duplicating the earlier experimental work, and it is now considered that the effect of arsenic has been under-estimated.

For most practical purposes, however, the presence of arsenic can still be ignored, but it is appreciated that significant error might be introduced in the examination of steels of the silicon-transformer type and those containing, say, less than 0.01 per cent. of phosphorus, when the arsenic content is greater than 0.1 per cent.

We have, therefore, adopted the expedient of removing the arsenic by introducing a simple modification into the recommended procedure. After solution of the sample in the hydrochloric acid - nitric acid mixture, as described in the first 3 lines of the "Procedure for Steels" on p. 142 [ending with the words "... sp.gr. 1.42 (Note 1)."], the following additional steps are taken—

Evaporate to dryness. Cool, add 5 ml of concentrated hydrochloric acid, sp.gr. 1.18, and 5 ml of hydrobromic acid, sp.gr. 1.46 to 1.49, and warm to dissolve the residue. Evaporate to dryness on a hot-plate, then cool.

At this stage the 5 ml of perchloric acid are added, and from this point the original procedure is followed.

Most of the metallurgical samples referred to in Table VII have been re-examined in this way and the phosphorus values obtained on the majority of these samples were the same as those originally reported; when lower values were obtained, none differed by more than 0.002 per cent. of phosphorus.

#### REFERENCE

1. Elwell, W. T., and Wilson, H. N., *Analyst*, 1956, **81**, 136.

RESEARCH DEPARTMENT  
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METALS DIVISION  
KYNOCHE WORKS, WITTON, BIRMINGHAM

RESEARCH DEPARTMENT  
IMPERIAL CHEMICAL INDUSTRIES LIMITED  
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BILLINGHAM, CO. DURHAM

W. T. ELWELL  
H. N. WILSON  
March 29th, 1957

## British Standards Institution

### NEW SPECIFICATIONS\*

- B.S. 2840:1957. General Purpose Maximum and Minimum Thermometers (Six's Pattern). Price 2s. 6d.  
B.S. 2841:1957. General Purpose Wet and Dry Bulb Hygrometer. Price 2s. 6d.  
B.S. 2842:1957. Whirling Hygrometer (Medium Size). Price 3s.  
B.S. 2843:1957. Spirit-in-glass Metal-sheathed Thermometer. Price 2s. 6d.  
B.S. 2846:1957. The Reduction and Presentation of Experimental Results. By J. T. Richardson, B.Sc. Price 10s.

### AMENDMENT SLIP\*

A PRINTED slip bearing amendments has been issued by the Institution, as follows—  
PD 2748—Addenda to the British Standards Yearbook 1957.

## Book Reviews

BIOCHEMICAL PREPARATIONS. Volume 4. Editor-in-Chief: W. W. WESTERFELD. Pp. viii + 108. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1955. Price \$3.75; 30s.

"Biochemical Preparations" has now become an institution, and with each succeeding volume the series becomes increasingly indispensable to biochemists interested in preparative work. Even so, how the material to be published in each volume is selected remains a mystery, and few biochemists are likely to be interested in the whole of the contents of this volume. Equally, however, there will not be many who find it completely devoid of interest.

In this latest volume methods are given for the preparation of twenty-two different substances, mostly by synthesis. These comprise galactose 1-phosphate, homogentisic acid, carnosine, histidinol, N-acetylimidazole, glycolaldehyde, sodium glyoxylate, tetracetyl-D-ribofuranose, L-argininic acid, DL-methionine sulphoxide, DL-methionine sulphone and DL-ethionine sulphone. The techniques employed are very varied and will be of interest to many organic chemists. Five substances, dipalmitoyl- $\alpha$ -lecithin,  $\alpha$ -lactalbumin,  $\beta$ -lactoglobulin and the enzymes, alcohol dehydrogenase and inorganic pyrophosphatase, are prepared by the extraction of suitable naturally occurring materials. Linoleic acid and its methyl ester are prepared from saponified safflower-seed oil—a method that preserves the natural configuration of the acid. The remaining three preparations are based on enzymic reactions, urocanic acid being prepared from histidine by treatment with histidine deaminase;  $\alpha$ -D-glucose 1-phosphate by phosphorolysis of starch in presence of phosphorylase and orthophosphate; and D-glutamic acid from the racemic acid by incubation with *Escherichia coli* cells or *Clostridium perfringens* cells. It is interesting to note that the enzymic preparation of  $\alpha$ -D-glucose 1-phosphate gives higher yields and is a simpler method to carry out than the synthetic method described in Volume 1.

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

The general pattern is identical with that followed in earlier volumes and in "Organic Synthesis," namely a preliminary section in which the principle of the method is discussed, then the detailed procedure and then a description of properties and purity of the product. In a final section, other methods of preparation are briefly referred to, with references. As usual, each preparation has been checked by an independent worker whose comments are given in footnotes.

Familiarity with the contents of "Biochemical Preparations" will greatly facilitate the task of the biochemist or his colleague in the organic chemical laboratory, if the substance in which he is interested happens to be there; obviously as the volumes mount up the series will become increasingly valuable as a storehouse of proved methods of preparation. F. A. ROBINSON

THE PRINCIPLES AND APPLICATIONS OF POLAROGRAPHY AND OTHER ELECTROANALYTICAL PROCESSES. By G. W. C. MILNER, M.Sc., F.R.I.C., A.Inst.P. Pp. xxviii + 729. London, New York and Toronto: Longmans, Green & Co. Ltd. 1957. Price 90s.

Despite, or perhaps because of, the steady annual outflow of about one thousand original papers on polarography, relatively few textbooks in English on polarography have appeared. This volume by Mr. G. W. C. Milner, who is already well known for his many contributions to polarographic literature, is the first British book on the subject. The chapters on practical polarography and metallurgical applications are the fruits of his wide experience gained in the Bragg Laboratory at Sheffield and in the Atomic Energy Research Establishment at Harwell.

The whole field of polarography and allied analytical techniques is surveyed in this ambitious volume, which is divided into four parts dealing with theory, instrumentation and technique (184 pages), inorganic polarography (284 pages), organic polarography (164 pages) and, finally, amperometric titrations (81 pages). The first part is strengthened by valuable chapters on polarographic theory and oscillographic polarography contributed by Mr. J. E. B. Randles of Birmingham University; Mr. Randles was a pioneer in the field of oscillographic polarography.

The book provides an excellent account of the present state of polarography and indicates the way in which the technique has spread to, and has found applications in, most branches of analytical chemistry. In all sections of the book adequate experimental details are given and comprehensive bibliographies containing literature references up to 1955 have been included. The many tables of polarographic data and the numerous figures are clear and easy to comprehend. The style of the book is occasionally laboured, but there are few printing errors.

This volume can be recommended to all analysts and chemical research workers, who require an up-to-date account of the scope and, also, the limitations of polarography. Students and physical chemists will find the chapters on theoretical polarography of value. All polarographers will want to keep a copy on their desk and will, further, wish to thank Mr. Milner for the immense amount of trouble that he has taken during the preparation of this volume. J. E. PAGE

MISES AU POINT DE CHIMIE ANALYTIQUE PURE ET APPLIQUÉE ET D'ANALYSE BROMATOLOGIQUE. Troisième Série. Edited by J.-A. Gautier. Pp. iv + 192. Paris: Masson et Cie. 1955. Price 1900 fr.

The third volume of these reviews or expositions is now available. Rather fewer subjects are dealt with and at somewhat greater length than in the two earlier volumes.

M. Lederer has contributed an article on recent developments in chromatography, which takes the form of a supplement to the book by M. and E. Lederer and brings this widely valued reference work up to date. Here, the relatively new technique of gas-liquid chromatography finds a place, of course, but is curiously omitted from another article that gives an otherwise comprehensive review of modern methods of gas analysis.

Food chemists will find interest in a critical review of the theory and practice of fat determination in milk and in an account of modern views on the rôle of trace elements in human and animal nutrition. A review of non-aqueous titration is included, but here a mistake in the equations chosen to illustrate the theory of acid-base reactions detracts somewhat from the clarity of the exposition.

The almost astronomical vastness of chemical literature to-day constitutes a serious problem; it is, indeed, one of those things that are always with us. Therefore it must be said that Professor Potter has done a valuable service in setting down some methods of tackling the problem, and having said that, it is perhaps inevitable that one should see certain omissions. Probably no two people would prepare the same list of reference works, but I do feel that the two volumes of Martindale's Extra Pharmacopoeia might well have been included. P. MORRIES

## Publications Received

OFFICIAL METHODS OF ANALYSIS (1957) OF THE SOCIETY OF LEATHER TRADES' CHEMISTS. Third Edition. Pp. viii + 200. Croydon: Society of Leather Trades' Chemists. 1957. Price 18s.

THE CHEMISTRY OF VEGETABLE TANNINS: A SYMPOSIUM. Pp. 160. Croydon: Society of Leather Trades' Chemists. 1956. Price 30s.

*Papers presented at a Symposium sponsored by the Society of Leather Trades' Chemists held at the University, Cambridge, April 12th to 13th, 1956.*

CRYSTAL STRUCTURES. Section IV. By RALPH W. G. WYCKOFF. Loose-leaf, 138 sheets. New York and London: Interscience Publishers Inc. 1957. Price \$7.00; 56s.

*Section IV consists of punched leaves for insertion into the binder of Volume II: it comprises chapters XI and XII.*

CAROTENE: ITS DETERMINATION IN BIOLOGICAL MATERIALS. By V. H. BOOTH. Pp. viii + 119. Cambridge: W. Heffer & Sons Ltd. 1957. Price 18s.

*Published under the auspices of The Society for Analytical Chemistry.*

SAFETY IN THE CHEMICAL LABORATORY. By H. A. J. PIETERS and J. W. CREYGHTON. Second Edition. Pp. xiv + 305. London: Butterworths Scientific Publications; New York: Academic Press Inc. 1957. Price 40s.; \$7.50.

SPECTROCHIMICA ACTA. Edited by E. H. S. VAN SOMEREN (London), H. W. THOMPSON (Oxford), V. A. FASSEL (Ames, Iowa, U.S.A.) and F. A. MILLER (Pittsburgh). Volume IX, No. 1, March, 1957. Pp. iv + 104. London, New York and Paris: Pergamon Press Ltd. Subscription A (normal) 147s., \$21.00 per volume; subscription B (for individual subscriber's own use) 73s., \$10.50 per volume.

*The scope of this journal has been considerably reorganised by the publishers.*

SUPPLEMENT 1957 TO THE BRITISH PHARMACEUTICAL CODEX 1954. Pp. xiv + 124. London: The Pharmaceutical Press. 1957. Price 27s. 6d.

MICROCHEMICAL JOURNAL. Edited by N. D. CHERONIS, J. A. MEANS, A. G. MISTRETTA, T. S. MA, A. A. BENEDETTI-PICHLER and B. ROSENFELD. Volume I, Issue 1, 1957. Pp. xii + 166. New York and London: Interscience Publishers Inc. Published under the auspices of The Metropolitan Microchemical Society. Subscription \$9.60 per annum.

*A new journal. (Two issues will be published in 1957.)*

AIR AND WATER POLLUTION: THE POSITION IN EUROPE AND IN THE UNITED STATES. *Project Nos. 136 and 145.* Pp. 218. Paris: The European Productivity Agency of the Organisation for European Economic Co-operation; London: H.M. Stationery Office; Washington, D.C.: O.E.E.C. Mission, Publications Office. Price 900 fr.; 18s.; \$3.00.

CHROMATOGRAPHY: A REVIEW OF PRINCIPLES AND APPLICATIONS. By EDGAR LEDERER and MICHAEL LEDERER. Second Edition. Pp. xx + 711. Amsterdam: Elsevier Publishing Co.; London: Cleaver-Hume Press Ltd.; New York: D. Van Nostrand Co. Inc. 1957. Price 72s.; \$11.50.

HETEROCYCLIC COMPOUNDS. Volume 6: SIX-MEMBERED HETEROCYCLES CONTAINING TWO HETERO ATOMS AND THEIR BENZO DERIVATIVES. Edited by ROBERT C. ELDERFIELD. Pp. viii + 753. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. Price \$25.00; 200s.