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Volume 90, No. 1070

May, 1965

Summaries of Papers in This Issue

Sodium Carbonate as a Primary Standard in Acid - Base Titrimetry

Report prepared by the Analytical Standards Sub-Committee

ANALYTICAL METHODS COMMITTEE
14 Belgrave Square, London, S.W.1.

Analyst, 1965, **90**, 251–255.

Nitrogen Factor for Veal

Report prepared by the Meat Products Sub-Committee

ANALYTICAL METHODS COMMITTEE
14 Belgrave Square, London, S.W.1.

Analyst, 1965, **90**, 256–257.

Rapid Analysis for Some Major Elements in Powdered Rock by X-Ray Fluorescence Spectrography

Commercially available X-ray fluorescence spectrographs permit rapid analysis for many of the major elements of silicate rocks. Their advantages are greatly reduced if laborious or highly skilled methods of sample preparation are required. A method is described involving cellulose-diluted rock powders as pressed pellets. This achieves a compromise between speed of preparation and accuracy of analysis for silicon, potassium, calcium, titanium, manganese and iron by using single calibration curves for silicate rocks of a wide lithological and chemical range. Several influences on the method are discussed, including the particle size of rock powders and of reductions in matrix effects by dilution with cellulose and by incorporating a heavy additive (bismuth oxide) with the diluent. Calibrations obtained are presented, and the application of the method tested with G–1 and W–1.

D. F. BALL
The Nature Conservancy, Bangor Research Station, Penrhos Road, Bangor, Caernarvonshire.

Analyst, 1965, **90**, 258–265.

An Improved Method of Pyrolysis in Gas Chromatography

An improved method of pyrolysis is described for the quantitative micro-analysis of non-volatile compounds by gas - liquid chromatography. The sample is pyrolysed in the glass capillary in which it is weighed. With up to 30 μg of sample an accuracy of at least ± 5 per cent. can be achieved.

The equipment used consists of an Oertling Q01 quartz-fibre microbalance and a Pye Panchromatograph fitted with a Pye pyrolysis unit and a flame ionisation detector, modified for use with radioactively labelled compounds.

F. G. STANFORD
U.K. Atomic Energy Authority, The Radiochemical Centre, Amersham, Bucks.

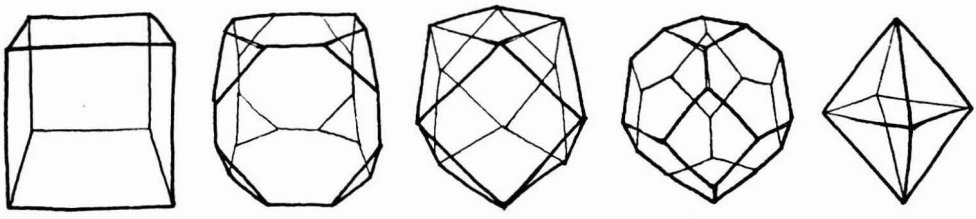
Analyst, 1965, **90**, 266–269.

The Absorptiometric Determination of Silicon in Water
Part V. Continuous Automatic Determination of "Reactive" Silicon

The use of the Technicon AutoAnalyzer for the continuous, automatic determination of "reactive" silicon in water has been studied. The instrument performed very reliably, and appears to be suitable for the continuous analysis of waters in power stations.

A. L. WILSON
Central Electricity Research Laboratories, Cleeve Road, Leatherhead, Surrey.

Analyst, 1965, **90**, 270–277.



progress in purity 1915 to 1965

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Thirty years ago 'AnalaR' specifications were introduced, describing more precise methods of testing and interpreting the tests in terms of maximum permitted limits of impurities. The first (1934) edition established standards for some 240 reagents. Four more editions have been published since—a sixth edition is in preparation—extending the range of 'AnalaR' reagents to 289, and successively incorporating, with advances in analytical methods, more rigorous procedures and more exacting standards.

Against the demands of specialised and instrumental methods of analysis still more highly purified reagents have been made available, as for spectroscopy and for micro-analysis, and for a number of specific individual applications.

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The Colorimetric Determination of Traces of Lead in Heat-resistant Nickel - Chromium Alloy Steel

Dibenzyldithiocarbamic acid is used for extracting lead from 0·5 M acid solutions of 25 per cent. nickel - 20 per cent. chromium steel before determination of the lead with dithizone. Three parts per million can be determined with an accuracy of ±1 p.p.m.

J. A. STOBART

National Physical Laboratory, Teddington, Middlesex.

Analyst, 1965, **90**, 278–282.

The Determination of Caesium-137 in Herbage and Soil

A method is described for determining caesium-137 in samples of herbage and soil. The sample, with added caesium carrier, is treated either by wet ashing with nitric and perchloric acids (herbage) or by fusion with alkali (soil). The resulting solution is acidified and passed through a column containing a mixture of ammonium dodecamolybdophosphate and asbestos. Caesium is retained on the column, together with some potassium, which is separated by selective elution. Finally, the ammonium dodecamolybdophosphate is dissolved and the caesium precipitated as the chloroplatinate, which is mounted and its β-radiation counted.

H. D. VANDERVELL and A. MORGAN

U.K. Atomic Energy Research Establishment, Harwell, Didcot, Berks.

Analyst, 1965, **90**, 283–289.

The Determination of Higher Alcohols in Potable Spirits: Comparison of Colorimetric and Gas-chromatographic Methods

Gas chromatography of brandies and whiskies shows that n-propanol, isobutanol, 2-methylbutan-1-ol and 3-methylbutan-1-ol comprise the major proportion of the higher alcohols. The furfural method for determining higher alcohols described in the Report of the Royal Commission on Whisky and Other Potable Spirits, 1909, gives results in excess of the sum of these alcohols determined by gas chromatography, but the method of the Association of Official Agricultural Chemists, which involves the use of *p*-dimethylaminobenzaldehyde, gives results that agree well with those obtained by gas chromatography.

D. D. SINGER and J. W. STILES

Laboratory of the Government Chemist, Ministry of Technology, Cornwall House, Stamford Street, London, S.E.1.

Analyst, 1965, **90**, 290–296.

The Ultrapurification of Hydrofluoric Acid

Short Paper

W. KWESTROO and J. VISSER

Philips Research Laboratories, N.V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands.

Analyst, 1965, **90**, 297–298.

The Colorimetric Determination of Isoniazid in the Presence of Sodium Aminosalicylate

Short Paper

S. C. ELLISTON and M. D. HAMMOND

The Analytical Laboratory, A. Wander Ltd., King's Langley, Herts.

Analyst, 1965, **90**, 298–300.

Spectrophotometric Determination of Beryllium with Beryllon III

Short Paper

P. PAKALNS and W. W. FLYNN

Australian Atomic Energy Commission Research Establishment, Lucas Heights, N.S.W., Australia.

Analyst, 1965, **90**, 300–303.

A Simplified Method for Determining Fibrous Residue in Wheatmeals and in Brown and Wholemeal Breads

Short Paper

H. ZENTNER

Bread Research Institute of Australia, Private Bag, P.O., North Ryde, N.S.W., Australia.

Analyst, 1965, **90**, 303–305.

Quantitative Determination of Aflatoxin in Groundnut Products

Short Paper

W. V. LEE

U.K. Milling Group Administration, Unilever Limited, Erith, Kent.

Analyst, 1965, **90**, 305–307.

The Determination of Carbon and Hydrogen in Organic Compounds Containing Mercury

Short Paper

T. F. HOLMES and A. LAUDER

Department of Chemistry, The University, South Road, Durham.

Analyst, 1965, **90**, 307–308.

Notice to Authors

THE Editor welcomes papers on all aspects of the theory and practice of analytical chemistry, fundamental and applied, inorganic and organic, including chemical, physical and biological methods. Papers are submitted to the Editorial Committee, who decide on their suitability for publication.

Intending authors should consult the current Notice to Authors, last published in full in *The Analyst*, 1965, **90**, 249, reprints of which can be obtained on application to The Editor, *The Analyst*, 14, Belgrave Square, London, S.W.1. All papers submitted will be expected to conform to the recommendations there laid down, and any that do not may be returned for amendment.

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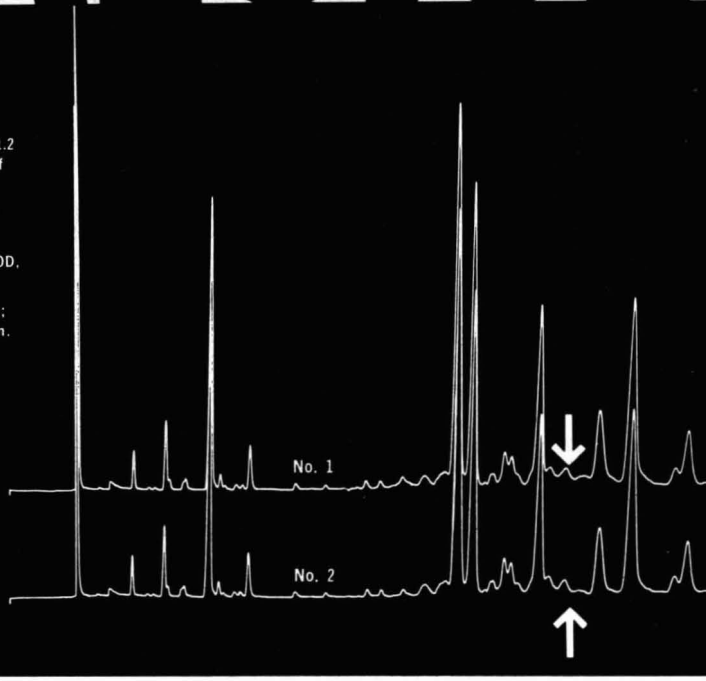

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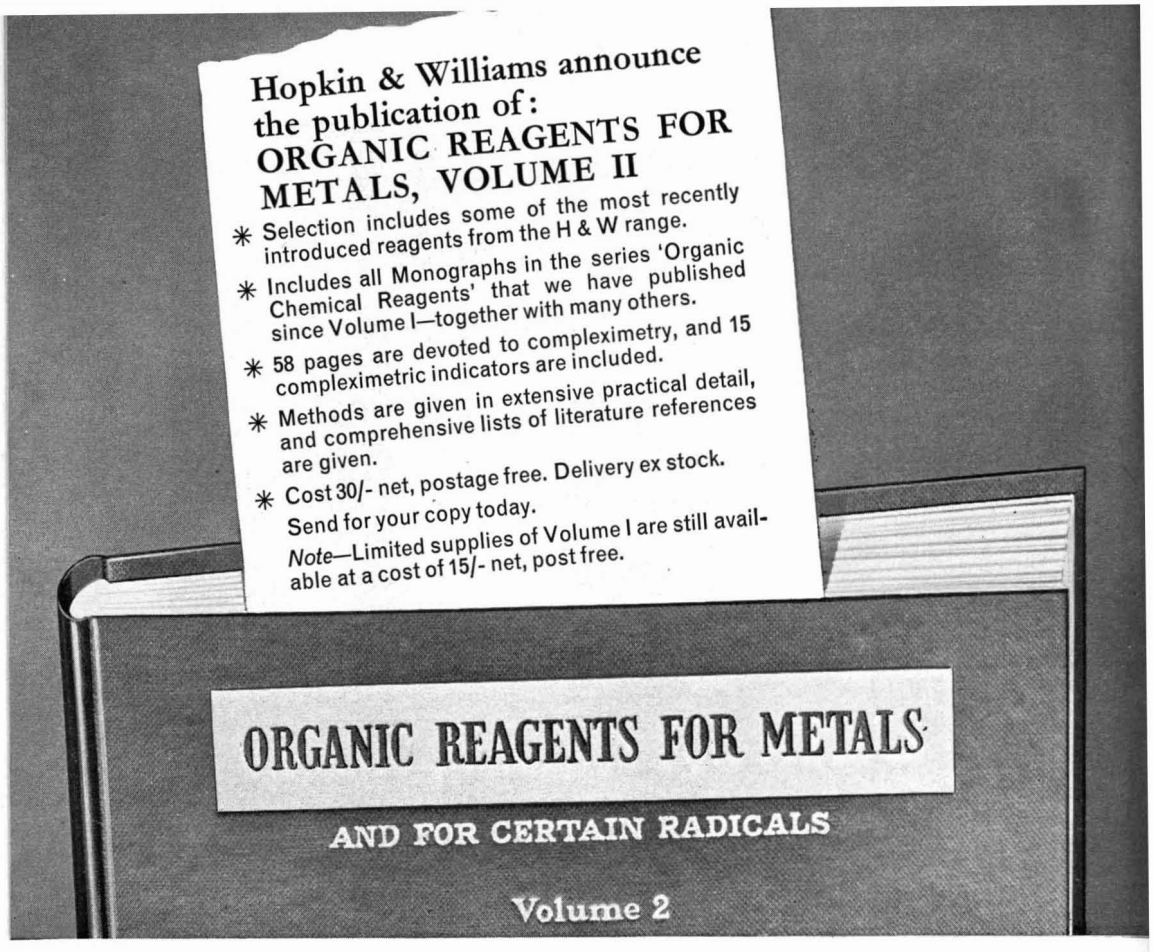

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THE ANALYST

Analytical Methods Committee

REPORT PREPARED BY THE ANALYTICAL STANDARDS SUB-COMMITTEE

Sodium Carbonate as a Primary Standard in Acid-Base Titrimetry

THE Analytical Methods Committee has received the following report from its Analytical Standards Sub-Committee. The report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

REPORT

At the request of the Analytical Chemistry Section of the International Union of Pure and Applied Chemistry the Analytical Methods Committee undertook, early in 1960, to carry out a critical examination of the various substances that have been proposed as primary standards for use in acid - base titrimetry. An *ad hoc* Panel under the Chairmanship of Professor R. Belcher was set up to review the request from I.U.P.A.C. and to suggest the constitution of a working sub-committee and draw up a preliminary programme of work. The Panel recommended that a sub-committee be appointed to investigate in detail the claims made for the use of certain established and "newer" standards with a view to recommending one or more as primary standards. The substances suggested by the Panel for detailed investigation were—

Established standards—

Sodium carbonate.
Sodium tetraborate decahydrate.
Potassium hydrogen phthalate.
Sulphamic acid.
Potassium bi-iodate.
Benzoic acid.

"Newer" standards—

Sodium hydrogen diglycollate.
2,4,6-Trinitrobenzoic acid.
4-Aminopyridine.
Tris-(hydroxymethyl)aminomethane.
Potassium hydrogen 3,5-dinitrobenzoate.

As at this time a Sub-Committee of the Microchemistry Group of the Society was about to begin a general investigation of titrimetric standards it was suggested to the Analytical Methods Committee that, with certain additions, the members of the Microchemistry Group's Sub-Committee should be invited to serve on the new Sub-Committee, which could subsequently take over the proposed general work on titrimetric standards.

The constitution of the Sub-Committee, which held its first meeting in June, 1960, is Mr. E. Bishop (Chairman), Mr. P. R. W. Baker, Mr. A. G. Hill, Mr. R. M. Pearson, Dr. W. I. Stephen, Mr. C. Whalley and Mr. J. T. Yardley. Subsequently, Mr. S. Andrus replaced Mr. Whalley, Dr. J. M. Skinner replaced Mr. Pearson and Dr. N. E. Topp* joined the Sub-Committee. Miss A. M. Parry was the original Secretary of the Sub-Committee; she was succeeded first by Dr. C. H. Tinker, then by Miss V. Lewis and finally by Mr. P. W. Shallis. The Sub-Committee's terms of reference are—

"To examine existing analytical standards and to select suitable substances."

The Sub-Committee first considered the list suggested by the *ad hoc* Panel and added to the list of "newer" standards hydrazine sulphate and cadmium acid *N*-hydroxyethyl-(ethylenedinitrilo)-*NN'N''*-triacetate (cadmium chelate). To establish which of the proposed standards should first be subjected to detailed experimental examination, the members

* Since deceased.

carried out critical surveys of the literature and consulted their combined experiences on all the substances in the list of established standards and also on hydrazine sulphate, sodium hydrogen diglycollate, 4-aminopyridine, tris-(hydroxymethyl)aminomethane and cadmium chelate. Theoretical analyses of the analytical chemistry of sodium carbonate, benzoic acid and certain other substances were made. Particular attention was given in these surveys to the following criteria of suitability, *viz.*—

(*a*) The substance should be readily purified.
(*b*) It should not be hygroscopic or efflorescent.
(*c*) It should be readily soluble.
(*d*) It should have a relatively high equivalent weight.
(*e*) It should not undergo any side reactions or colour change that would interfere with the titration or the indicator.
(*f*) The elements in the substance should be such that disturbance of the natural isotopic abundance would not materially affect the molecular weight.
(*g*) It should preferably be monobasic, completely ionised and suitable for direct titration.

The Sub-Committee evolved the classification given below for application in its work.

A. Reference or atomic-weight standard (*e.g.*, atomic-weight silver).
B. Ultimate standard; a substance that can be purified to virtually atomic-weight standard.
C. Primary standard; a commercially available substance of purity 100 $\pm$ 0·02 per cent.
D. Working standard; a commercially available substance of purity 100 $\pm$ 0·05 per cent.
E. Secondary standard; a substance of lower purity that can be standardised against a grade C material.

SURVEY OF THE LITERATURE ON PROPOSED STANDARDS—

From the critical survey of the proposed standards no single one emerged with an outstanding claim to first consideration, but sodium carbonate and sodium tetraborate decahydrate appeared the most promising.

Sodium carbonate can be obtained in a pure state (grade C or even B), but some doubt exists about the precision of results obtained by its use, which involves the liberation of carbon dioxide. It is also necessary to dry it before use, and it may be hygroscopic. Sodium tetraborate can also be obtained in a pure state (grade C or B), but suffers the disadvantage of being hydrated, thereby necessitating storage in a hygrostat.

Potassium hydrogen phthalate is probably not commercially available with a purity better than grade D, and is limited in its application by its low second ionisation constant. Different opinions are held on the method of preparation and the purity of sulphamic acid, but it was considered that the purity of the commercially available material was grade D or possibly grade C. Further, it was thought that there are theoretical disadvanatages attendant on the use of a material that decomposes in solution, even though its titre remains the same. Potassium bi-iodate is a stable non-hygroscopic substance; it has a high equivalent weight and is bi-functional. However, some doubt exists about its stoicheiometry and its purity is regarded as being in grade D. Benzoic acid is undoubtedly available in a highly pure state (grade B), but it suffers the disadvantages of being a weak acid not particularly soluble in water.

As little published information was available on the other substances included in the survey it was realised that further work would be necessary before a true assessment of their value in the Sub-Committee's scheme could be made. Work was already in hand in the laboratories of some members on certain of these substances, but it was decided that, as no definite evidence was available showing that any one of them was more promising than sodium carbonate or sodium tetraborate, no collaborative investigation would be undertaken at this stage. It was, however, agreed that, if practicable, all proposed standards would eventually be investigated and related to the Sub-Committee's recommended primary standards.

Of the substances considered the most promising, work was begun first on sodium carbonate, and it was decided that as few laboratories would have the facilities for working at the level of grade A or B the Sub-Committee would concentrate on work at the grade C level.

In this Report a brief account of the various stages of the work and of the conclusions reached are given. The experimental procedures used in the assays require facilities and conditions not commonly available in many laboratories, and it is intended that the descriptions of these and the detailed results obtained will be given at a later date.

Assay of sodium carbonate

Two possible methods for the high-precision assay of sodium carbonate were considered, one involving relation to grade A silver through titration against hydrochloric acid and the other titration against benzoic acid. As both methods appeared suitable it was decided that both should be used, and detailed procedures were drawn up. The titrations were to be of the partial-neutralisation type to alleviate the difficulties of carbon dioxide removal; for the titration against hydrochloric acid, 50 ml of 1·0 M hydrochloric acid were to be dispensed from a weight burette and allowed to react with 99·8 per cent. of the theoretical amount of sodium carbonate and the titration of the 0·2 per cent. excess of hydrochloric acid completed with 0·05 M barium hydroxide, itself standardised against the hydrochloric acid. The hydrochloric acid was to be standardised against grade A silver. For the titration against benzoic acid, 2·5 g of sodium carbonate were to be neutralised with a 0·25 per cent. excess of benzoic acid and the titration completed with 0·05 M barium hydroxide, itself standardised against the benzoic acid.

For the collaborative assays carried out by these methods, common samples of zone-refined benzoic acid and of 1·0 M hydrochloric acid were to be used.

Assay against benzoic acid—

Before beginning collaborative assays, members carried out some preliminary tests on stock materials by the proposed method. Immediately some members reported evidence of loss of benzoic acid during removal of carbon dioxide. An investigation carried out by one member showed this loss to be about 2 mg per hour at 60° C in a stream of nitrogen, and it was decided at this stage to make no further use of the assay against benzoic acid.

Later, when satisfactory results had been obtained by the assay against hydrochloric acid, interest in the benzoic acid method was revived. Modifications aimed at avoiding the loss of benzoic acid were introduced and the method was used to check the purity of samples of sodium carbonate already assayed against hydrochloric acid. However, evidence of loss of benzoic acid was still encountered, and an investigation of the loss in one laboratory confirmed the earlier findings; further, the spread of results for the assay of sodium carbonate was several times greater than that by the hydrochloric acid method. It was concluded that, although the purity of benzoic acid was not in doubt, the difficulties encountered in its use were too great for complete reliance to be placed on the results obtained, and the method was therefore abandoned in the present context.

Assay against hydrochloric acid—

Standardisation of the hydrochloric acid—Nominally 1·0 M hydrochloric acid was prepared in one laboratory from constant-boiling hydrochloric acid and its concentration checked in that laboratory by a published method.[1] Before the acid was circulated to the other collaborators, a sample was sent to one of them and the concentration checked by reference to silver.[2] As the concentrations reported by the two laboratories differed by about 0·2 per cent., a further check was carried out in the two laboratories, the difference between the results on this occasion being 0·14 per cent., which was considered greater than would normally be expected between laboratories.

It was first thought that the variations might be due to the different methods of standardisation used in the two laboratories or, more likely, to sorption on the conditioned polythene containers in which the acid was stored and transported. However, an investigation in one laboratory showed that water was evaporating past ill-fitting stoppers in some of the bottles, thereby causing a slow increase in titre.

To overcome this difficulty it was decided that for the collaborative assays laboratories should prepare their own acid and standardise it before use by reference to silver,[2] a common

sample of grade A silver being used for the purpose. The silver was of "five nines" grade and analysis at Imperial Metal Industries (Kynoch) Ltd. revealed gas contents of 25 p.p.m. (by weight) of oxygen in the untreated silver (28, 35 and 30 p.p.m. in the treated[2] material), 2 p.p.m. of hydrogen and 10 p.p.m. of nitrogen.

Collaborative assays—As no inherent difficulties were experienced in trials of the method, a series of collaborative assays was planned. Four samples of sodium carbonate (two from each of two sources) were distributed and the assays were carried out against hydrochloric acid prepared and standardised in each laboratory. To obtain the maximum information from as few assays as possible, a Latin Square was designed, and the results when inserted in this square indicated a significant high bias in the results from one laboratory.

A further series of assays was carried out on four new samples (two from each of the same two sources) and the Latin Square appraisal was again used. Good agreement within samples was obtained, but the results indicated that approximately 0·04 per cent. of the samples was unaccounted for in the assay. Examination with a Hilger medium-quartz spectrograph and copper electrodes indicated the presence in the two samples from one source of calcium (0·012 and 0·016 per cent.) and silicon (0·002 and 0·003 per cent.); no other impurities were detected. The samples from the other source gave on examination 0·014 per cent. of calcium and evidence of the presence of potassium and aluminium. As it was possible that occluded water could make up the difference, it was decided to test for water by nuclear magnetic resonance spectroscopy; the technique, however, proved to be insufficiently sensitive for use at this level.

It was concluded that materials from the two sources so far examined did not meet the Sub-Committee's requirements for a grade C standard.

Examination of sodium carbonate from a further commercial source—

Spectrographic examination of a sample of sodium carbonate from a further commercial source had indicated only one faint line, which might have been due to aluminium. This sample, which was more than 25 years old, had a different physical appearance from the earlier samples tested, it being in the form of free-flowing fine granules whereas the others had all been powders.

Two further samples of sodium carbonate from different batches were obtained from the same source and collaborative assays on all three samples were carried out in four laboratories. In all, results of 33 assays against hydrochloric acid were reported on these samples. These results were all within the range 99·980 to 100·010 per cent., the mean being 99·993 per cent. with a standard deviation of $\pm 0{\cdot}005$.

It was apparent that sodium carbonate from this commercial source met the requirements of a primary standard (grade C) in the Sub-Committee's classification. Members were aware that not all commercial sources of sodium carbonate had been investigated, but a programme of work involving an investigation of this magnitude was considered impracticable. However, it was considered that it could be stated with confidence that sodium carbonate suitable for use as a primary standard was available commercially.

Laboratory preparation of grade C sodium carbonate—

After the work on commercially available sodium carbonate had been completed, one member of the Sub-Committee was of the opinion that sodium carbonate satisfying the requirements of a grade C standard could be prepared in the laboratory by a method involving ignition of analytical-reagent grade sodium hydrogen carbonate that had been recrystallised from water. Full details of the method of preparation are given in the Appendix (see p. 255).

Two samples of sodium carbonate were prepared by this method in two laboratories and were assayed on a collaborative basis. The results of 13 assays, which were all within the range 99·985 to 100·01 per cent., had a mean of 99·996 per cent. with a standard deviation of $\pm 0{\cdot}008$.

The results indicate that sodium carbonate prepared by the method described in the Appendix does in fact meet the Sub-Committee's requirements for a primary standard.

Conclusions

As a result of the collaborative work described in the Report extending over a period of 4 years the Sub-Committee recommends that sodium carbonate is a suitable substance for use as a primary standard.

Further, it is known that at least one commercial source of sodium carbonate that is within the required assay limits for a primary standard, *viz.*, 100 ± 0·02 per cent., exists, and that sodium carbonate prepared as described in the Appendix is also satisfactory.

The standard deviations on the results of the two final assays indicate that the analytical procedure used affords a certainty of better than 0·01 per cent., and is well within the requirements for materials of grade C.

Appendix

Laboratory preparation of primary-standard sodium carbonate

Starting material—

Sodium hydrogen carbonate—Analytical-reagent grade.

Procedure—

Add gradually and with frequent stirring 769 g of the analytical-reagent grade sodium hydrogen carbonate to 3 litres of distilled water at 86° ± 1° C in a hard-glass 4-litre beaker; maintain the solution at this temperature until all the solid has been added and has dissolved. Remove the beaker from the source of heat and stir the solution until the temperature falls to 75° C and a small crop of crystals is precipitated. Pass the solution, without further cooling, under suction through a close-grained filter-paper supported on a previously warmed large Buchner funnel. Cool the filtrate quickly and with stirring until the temperature falls to 18° to 20° C and the main crop of crystals is separated. Collect the crystals on a Whatman No. 541 filter-paper supported on a Buchner funnel, and remove as much of the mother liquor as possible by suction. Wash the crystals on the filter-paper once with a small amount of ice-cold distilled water, and dry them as completely as possible under suction. Transfer the damp crystals to a porcelain basin, and dry them by heating at 100° C; stir the mass from time to time during the drying. Lightly grind the dried crystals to a powder, mix the powder thoroughly, and convert it to sodium carbonate by heating to constant weight at 270° ± 10° C in a platinum basin.

References

1. Cox, S. J., Johnson, W. C., Newman, E. J., and Yardley, J. T., *Analyst* 1961, **86**, 464.
2. Strouts, C. R. N., Wilson, H. N., and Parry-Jones, R. T., *Editors*, "Chemical Analysis: The Working Tools," Clarendon Press, Oxford, 1962, Volume I, p. 200 (see also *Analyst*, 1950, **75**, 577).

Analytical Methods Committee

REPORT PREPARED BY THE MEAT PRODUCTS SUB-COMMITTEE

Nitrogen Factor for Veal

THE Analytical Methods Committee has received the following report from its Meat Products Sub-Committee. The report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

REPORT

The Meat Products Sub-Committee of the Analytical Methods Committee responsible for the preparation of this report was constituted as follows: Dr. S. M. Herschdoerfer (Chairman), Mr. S. Back, Mr. P. O. Dennis, Mr. J. R. Fraser, Mr. H. C. Hornsey, Dr. A. J. Kidney, Mr. T. McLachlan, Dr. R. A. Lawrie, Dr. A. McM. Taylor and Mr. E. F. Williams, with Miss V. Lewis as Secretary.

As in its earlier reports,[1,2,3,4] the Sub-Committee agreed to base on Stubbs and More's method its recommendations for the determination of the raw fresh-meat content in products made from veal. Six laboratories (see below) collaborated in the collection of values for the nitrogen content of veal, and the results are summarised in Fig. 1.

The term "veal" covers a considerable range of carcase weights or ages of animals at slaughter. Generally, this means animals up to 6 months old or of a live weight below 220 kg (484 lb).

In its investigations on other types of meat, the Sub-Committee found it necessary to distinguish between different cuts. However, the investigations on veal by laboratories A and C showed no consistent differences between cuts, and, further, veal is normally used entire in manufacture.

Considerable amounts of veal are imported into this country as frozen veal. For the analysis of frozen veal the Sub-Committee issued the following instructions—

> Veal as used for manufacturing purposes is imported in hard-frozen blocks consisting of several whole sides, together with some part sides. Sampling should be carried out by partial thawing to the stage at which it is possible to separate the sides without allowing complete melting and consequent separation of drip. With a normal commercial pack weighing about 70 lb this can be done by maintaining it for 2 days at 45° to 50° F. The separated side should then be comminuted entire, thoroughly mixed, and sampled for analysis.
>
> Any alternative method of thawing that avoids loss of drip may be used. If a significant amount of drip is formed during thawing, it should be measured, analysed separately, and an appropriate proportion allocated to each individual component of the pack.

RECOMMENDATION

The Sub-Committee recommends an average nitrogen factor of 3·35 for veal as the best compromise for general use.

ACKNOWLEDGMENT

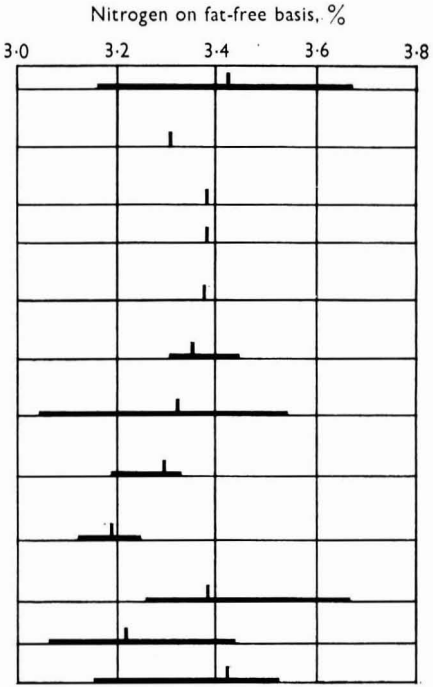
The Sub-Committee thanks those listed below for their help and communications—

British Food Manufacturing Industries Research Association.
Crosse & Blackwell Ltd.
Danish Meat Research Institute, Roskilde.
C.S.I.R.O., Brisbane.
J. Sainsbury Ltd.
T. Wall & Sons (Meat and Handy Foods) Ltd.

REFERENCES

1. Analytical Methods Committee, *Analyst*, 1961, **86**, 557.
2. ——, *Ibid.*, 1963, **88**, 422.
3. ——, *Ibid.*, 1963, **88**, 583.
4. ——, *Ibid.*, 1964, **89**, 630.

		Laboratory	No. of samples	Range	Mean	
FRESH	Weight of sides (including bone) 12 to 23 lb	A	5	3·16 to 3·68	3·42	
	Aberdeen Angus × Ayrshire: Age 3 days: carcase weight 40·5 lb	B	1	—	3·31	
	Age 6 weeks: carcase weight 109 lb	B	1	—	3·39	
	Shorthorn: Age 15 days: carcase weight 74 lb	B	1	—	3·39	
	Angus × Guernsey: Age 3 weeks: carcase weight 66 lb	B	1	—	3·38	3·34
	Age 120 to 204 days: carcase weight 202 to 275 lb	C*	6	3·31 to 3·45	3·36	
	Australian Illawarra Shorthorn: Age 30 to 180 days	D†	24	3·04 to 3·55	3·33	
	Australian: mean of 3 samples taken from commercial boning lines	D	5	3·19 to 3·33	3·30	
FROZEN	Weight of sides (boneless) 7·7 to 13·9 lb	A	5	3·12 to 3·24	3·19	
	—	E	27	3·26 to 3·67	3·39	3·33
	English	F	12	3·06 to 3·44	3·22	
	Australian	F	6	3·15 to 3·53	3·42	



* Figures based on analysis of 15 to 18 individual muscles.

† Figures based on analysis of muscles in 3 groups, calculated to whole edible meat.

Fig. 1. Nitrogen contents of fresh and frozen veal. Horizontal lines represent the range of nitrogen contents, short vertical lines indicate the average values

Rapid Analysis for Some Major Elements in Powdered Rock by X-Ray Fluorescence Spectrography

By D. F. BALL

(*The Nature Conservancy, Bangor Research Station, Penrhos Road, Bangor, Caernarvonshire*)

Commercially available X-ray fluorescence spectrographs permit rapid analysis for many of the major elements of silicate rocks. Their advantages are greatly reduced if laborious or highly skilled methods of sample preparation are required. A method is described involving cellulose-diluted rock powders as pressed pellets. This achieves a compromise between speed of preparation and accuracy of analysis for silicon, potassium, calcium, titanium, manganese and iron by using single calibration curves for silicate rocks of a wide lithological and chemical range. Several influences on the method are discussed, including the particle size of rock powders and of reductions in matrix effects by dilution with cellulose and by incorporating a heavy additive (bismuth oxide) with the diluent. Calibrations obtained are presented, and the application of the method tested with G–1 and W–1.

X-RAY fluorescence spectrography by commercially available instruments does not currently permit total rock analysis, since quantitative determination of elements lighter than magnesium is impossible, or at least inaccurate, at normal concentrations. Magnesium itself is at the limit of the range of commercial instruments. The technique can be used for analysing major, minor and trace elements heavier than magnesium much more rapidly than is possible by chemical means, with an accuracy at least comparable to that of typical chemical analyses.[1] It can thus be applied to studies demanding a knowledge of the distribution of such elements in rocks and other silicate materials. It is important that the time or degree of skill required in sample preparation is kept to the essential minimum for each specific problem, in order not to detract from the advantages inherent in the instrument of speed and relatively unskilled operation. It has frequently been stated[2 to 7] that fusion techniques are essential for accurate quantitative analysis of rocks differing widely in composition and lithology. Very recent work has supported this.[1] However, fusion techniques are not well suited to semi-skilled handling of large numbers of samples. Our work requires reasonably accurate and rapid analysis for some major elements, and it was therefore considered that further study of the direct use of powdered-rock analysis was justified.

Considerations of Sample Preparation

Powders have previously been used packed loosely,[8,9] or under pressure[10,11] into holders, or briquetted with added binders or diluents, or both.[4,12] There is difficulty in handling and reproducibly packing loose powders, so that briquetted discs are preferred. In order to ensure stability of discs under vacuum, to increase their mechanical strength, and to buffer differences in sample composition by dilution with a standard additive, the discs are made of a mixture of rock powder and powdered cellulose (Whatman standard grade).

The problems of quantitative rock-powder analysis arise mainly from two factors—

(*i*) Differences in particle size between samples.

(*ii*) Differences in general chemical composition, usually termed "matrix" effects.

Bernstein[13] has pointed out that if the powders are of a standard limited range of particle size, effect (*i*) is eliminated. This is so for samples defined as fractions by size, *e.g.*, silt and clay fractions. In general it is a slow and difficult process to obtain a closely defined and limited particle-size range by hand-grinding from rocks and minerals of varying hardness. Equipment consisting essentially of a combined automatic ball-mill and sieving system designed by Pitchford[14] is not generally available, and this and other mechanical automatic grinders are costly.

The magnitude of the particle-size effect was studied for calcium in the work reported here by using a series of ground pure limestone and precipitated calcium carbonate samples

kindly made available by the British Whiting Research Council (now Whiting and Industrial Powders Research Council). A compromise has to be adopted between the opposing requirements for minimising effects (*i*) and (*ii*). Greater dilution reduces matrix-effect differences and increases the intensity of the X-ray count per unit element, although it naturally reduces the total intensity of radiation from the sample disc. However, greater dilution increases the particle-size effect by increasing the inhomogeneity of powder in the diluent. If powdered rock is used without dilution as a briquetted disc, the close-packed powder forms a uniform sample. Very fine grinding in this instance is required mainly to ensure sample homogeneity. Where the rock powder is dispersed in a diluent, size is of greater importance,[4,15] because if a given amount of powder is present as a large number of small particles, all may be effective in emitting fluorescent radiation, but if present as a small number of large particles, only the outer zone of each particle is effectively sampled. The magnitude of this effect is greater for easily absorbed, long-wavelength radiation from light elements than from the shorter wavelengths emitted by heavy elements. The study of calcium analysis in calcium carbonate powders took into account different levels of dilution and particle-size ranges. Table I shows the results obtained, the particle size being indicated as an arithmetic mean equivalent spherical diameter (e.s.d.), on an assumption that the range of sizes in each fraction was a continuous uniform scatter between the known limiting sizes. This is unlikely to be true, and, therefore, the differences between size grades are smoothed out, but the general trends represent well what is met in practical powder analysis.

TABLE I

RELATIVE CALCIUM K_α INTENSITIES* FOR CALCIUM CARBONATE POWDERS OF DIFFERENT MEAN PARTICLE SIZE AND DILUTION FOR TUNGSTEN RADIATION

Mean particle size, μ	Ratio of sample to cellulose					
	1 to 19	1 to 3	1 to 2	1 to 1	3 to 1	1 to 0
1	100	100	100	100	100	100
5	96	100	100	99	100	100
25	80	96	96	95	94	97
56	52	73	77	83	91	93
109	42	66	71	79	89	95

* Calcium K_α intensity as percentage of the 1-μ size fraction count at each dilution.

The greater effect of particle size on X-ray emission at greater sample dilution can be seen in Table I. Although extreme dilution is, as stated, preferable to minimise matrix effects, it is not practicable unless particle size can be strictly controlled. If fractions defined by size, as with clays, are used, large dilutions are practicable and may be preferable. Small dilutions produce mechanically weak discs and increase possibilities of error due to matrix effects. A dilution of 1 to 2 or 1 to 3 for sample to cellulose is a reasonable compromise, that of 1 to 2 being adopted as standard practice. If powders are produced having a mean particle size not greater than 25 μ, then the extreme error in calcium analyses possible is of the order of 5 per cent. of the X-ray count obtained, between samples of 1 and 25 μ mean e.s.d. A mean particle size of 25 μ is closely approached by grinding all rocks to pass a 300-mesh (53-μ aperture) sieve. The range in mean particle size between two samples subject to the standard grinding procedure described below is likely to be much smaller than from 1 to 25 μ mean e.s.d. That this is so is shown empirically by calibration curves obtained with such samples both for calcium and for potassium in which particle-size effects are greater.

Errors resulting from matrix effects may be overcome by internal-standard methods, but these are not convenient if the determination of more than one element in a set of samples is required. Calculations from mass-absorption data are also complex in general work that covers several elements. It was therefore preferred to aim at the simplest technique, *viz.*, the use of single calibration curves from analysed standard rocks of a wide lithological range.

Recent work[6] suggested that a further improvement of the reduction in matrix effects produced by dilution with, *e.g.*, cellulose, was brought about by adding a standard amount of a heavy absorbing element. This amount should not be sufficient to reduce too greatly the overall intensity of emission analysed for the elements being determined. Lanthanum oxide, as used in the work referred to, was found to be somewhat unstable mechanically in

pressed cellulose discs, which flaked or produced a blistered surface liable to turn into powder within a period of days. It is possible to use bismuth oxide (Bi_2O_3) as an alternative heavy absorber. Bismuth interferes with the determination of chromium, rubidium, zirconium, tin and antimony, but does not interfere with the major elements currently of interest to us, *viz.*, silicon, potassium, calcium, titanium, manganese and iron.

The influence of additions of bismuth oxide (B.D.H. laboratory reagent, <300 mesh) on the reduction of matrix effects has been briefly tested at two concentrations with iron $K\alpha$ radiation. The results are given in Table II for a standard amount of iron with a change of 80 per cent. in sample composition from cellulose, either plain or with additive, to silica at a 1-to-2 dilution for sample to cellulose.

TABLE II

INFLUENCE OF BISMUTH OXIDE ADDITIVE ON IRON $K\alpha$ COUNTS

Fe_2O_3, g	Cellulose, g	Bi_2O_3 in cellulose, per cent.	SiO_2, g	Counts $\times 10^{-3}$*
0·2	2·8	nil	nil	170
0·2	2·0	nil	0·8	113
0·2	2·8	10	nil	90
0·2	2·0	10	0·8	79
0·2	2·8	20	nil	57
0·2	2·0	20	0·8	54

* At uniform operating conditions.

As expected, the reduction in matrix effect of increasing heavy additive is seen. The count-rate fall caused by the matrix change from cellulose to silica is 34 per cent., 12 per cent. and 5 per cent., respectively at 0, 10 per cent. and 20 per cent. of bismuth oxide additive. From this aspect, the use of 20 per cent. of bismuth oxide additive is most effective, and this should be used when count rates are sufficiently high for loss in sensitivity to be ignored. However, since this loss of sensitivity was considered probably to be greater than acceptable for the lighter elements in the present work, 10 per cent. of bismuth oxide was used in the cellulose diluent. This level reduces the calcium count at a dilution of 1 part of rock powder to 2 parts of cellulose by about 25 per cent. from that obtained with a plain cellulose diluent. (The cost of the bismuth oxide added is approximately $\frac{1}{3}$d. per sample at the 10 per cent. level.)

METHOD

ROUTINE PREPARATION PROCEDURE—

In the adopted routine preparation procedure for rock analysis, approximately 20 g of rock chips were crushed initially in a tool-steel mortar in a hand-operated hydraulic press until all the crushed material had passed a 16-mesh (1-mm) sieve. A suitable small sub-sample (approximately 5 g) of the crushed material taken from a sample splitter was ground by shaking it in high-alumina ceramic vials[16] with 99 per cent. alumina ball-pestles. Four or six vials at a time were conveniently accommodated in a holder in a paint-mixer that provided a multi-way shaking action.[16] Shaking was interrupted at about 20-minute intervals so that the powder might be passed through a 300-mesh sieve. Soft rocks may be completely ground in one 20-minute period, but any material coarser than 300 mesh is returned for further grinding. A maximum of 1 hour total grinding time ensures complete grinding of virtually all rocks, and the sieving at intervals gives some protection against excessive grinding of soft minerals to very fine particle size. After the ground powder had been thoroughly mixed to ensure a homogeneous sample, 1 g of powdered rock was added to 2 g of Whatman powdered cellulose containing 10 per cent. by weight of bismuth oxide (previously mixed in a bulk supply). The mixture was again shaken in the paint-mixer in batches of 24 to 36 samples at a time for 40 minutes in polythene vials containing 2 × $\frac{1}{4}$-inch diameter methacrylate ball-pestles. The mixed material was then pelleted in a steel mould in the hydraulic press as previously described for plant material[17] to give sample discs of $1\frac{1}{4}$-inch diameter and approximately $\frac{1}{12}$-inch thickness. Under a pressure of 6000 p.s.i., strong sample discs are produced; these can be identified by numbers written on their edge and may be conveniently stored in slide-boxes in card and Cellophane holders.

OPERATING CONDITIONS OF SPECTROGRAPH—

The X-ray spectrograph used was a Hilger & Watts Flurovac, with an A.E.G. tungsten-target, side-window X-ray tube. Scintillation and gas-flow counters were both used, their outputs combined in a pre-amplifier. All determinations were made under vacuum, with pulse-height analysis used for lighter elements. Table III gives normal operating conditions. An analysing crystal of pentaerythritol, now available commercially, was used for light elements instead of the more usual ethylenediamine ditartrate, because it gives a higher count-rate. There is only a slight difference in *d*-spacing between these two crystals, so that angular spacings for the elements do not differ greatly.

TABLE III

OPERATING CONDITIONS FOR FLUROVAC

Element	Tube conditions	Collimator slits	Crystal	Pulse-height analysis	Count-rate of main K_α peak (counts per second at stated percentage)
Silicon	50 kV, 20 mA	Coarse (0·02 inch)	Pentaerythritol	Yes	330 (100% SiO_2)
Potassium	50 kV, 20 mA	Coarse	Pentaerythritol	Yes	800 (5·5% K_2O)
Calcium	50 kV, 20 mA	Fine (0·01 inch)	Pentaerythritol	Yes	1700 (20% CaO)
Titanium	50 kV, 20 mA	Coarse	LiF	No	2200 (3·5% TiO_2
Manganese	50 kV, 20 mA	Fine	LiF	No	240 (0·25% MnO_2)
Iron*	50 kV, 20 mA	Fine	LiF	No	1300 (12% Fe_2O_3)

* For iron, an aperture cutting the fluorescent radiation to about one-twelfth of full output is used between sample and slits, and tube output is maintained.

The Flurovac uses a monitoring system, by means of which the analytical counts are accumulated over the time required to make a standard count on a reference channel that monitors the primary beam. At the reference setting normally used (10^5 counts), actual counting time is approximately 30 seconds for all elements. Analytical time per sample per element is of the order of 1 minute, allowing for sample change-over and vacuum pumping of the sample chamber.

RESULTS

The applicability of the procedure to the determination of silicon, potassium, calcium, titanium, manganese and iron has been tested by using a range of silicate-rock samples of varied petrological and mineralogical character, from different analytical sources. These samples include granite, rhyolite, dolerite, basalt, calcareous and non-calcareous shales, silica refractories and glass, from three sources: the United States Bureau of Standards; Department of Mineralogy and Petrology, University of Cambridge; and The Geological Survey of Great Britain. Results obtained from this range are shown in Table IV for silica, potassium oxide, calcium oxide, titanium dioxide, manganese oxide and total iron as Fe_2O_3, oxide percentages being quoted as in the general convention for rock analysis. Most results represent independent determinations, although a few are for mixtures where needed to improve coverage of the range. If calibrations are drawn for mixtures between two end-members, there is an almost perfect correlation of content to X-ray counts. Thus the closeness of fit obtained between calibration curves for these rocks and for refractories of different sources and chemistry is, as also indicated by Hooper,[1] as much a test of the chemical analyses and, of course, of sampling procedure as of the X-ray technique used. A more independent assessment of the latter is, however, obtained by using a range of individual samples than with calibrations drawn from mixtures of two end-members.

It is usual to carry out a rapid check count on the two sides of each sample disc for the first element determined for a batch of samples, *e.g.*, for calcium. It is found that homogeneity of mixing is usually such that the two counts do not differ by more than the X-ray counting-error, which with the count-rates obtained, is generally of the order of 0·5 per cent. If there is a greater difference between the count on the two sides of a sample disc than 1 to 2 per cent., a replicate of the sample may be made, or a mean count of the two sides taken for all elements. This latter procedure is used for silica, for which minor inhomogeneity has a greater effect. The X-ray counts for silica in Table IV are the mean of single counts on each side of the sample disc. Poor replication is rare with the mixing procedure used, and the calibrations shown for other elements in Table IV were obtained on single 30-second counts of one side of single discs of each sample, in order to reproduce routine procedure. If a comparison is required between sediments of high water or organic-matter content (say greater

TABLE IV

RESULTS OF X-RAY SPECTROGRAPHIC CALIBRATION ANALYSES OF STANDARDS OF KNOWN COMPOSITION

Contents are quoted on an air-dry basis, except where noted

Sample	Source	SiO_2			K_2O			CaO		
		percentage content	X-ray count	ratio of X-ray count to percentage content	percentage content	X-ray count	ratio of X-ray count to percentage content	percentage content	X-ray count	ratio of X-ray count to percentage content
Rhyolite 708	*a*	73·8	6463	88	4·6	18885	4105	0·32	839	2622
Rhyolite 169	*a*	72·8	6370	88	4·1	18216	4443	0·92	2567	2725
Shale 1056	*b*	70·4*	6196	88	2·98*	13302	4464	0·24	939	3914
Calcareous Shale 1424	*c*	53·2†	4765	90	1·2†	5717	4764	19·5	51424	2637
Calcareous Shale 1425	*c*	58·8†	5200	88	3·1†	13967	4505	5·5	11408	2074
Dolerite, Carnmoney	*d*	49·1	3719	76	0·51	2390	4686	9·99	23832	2386
Basalt, Kilauea 1921	*d*	49·1	3510	71	0·52	2439	4690	11·02	26372	2393
Basalt, Kilauea 1960	*d*	48·8	2988	61	0·51	2415	4735	9·59	22315	2327
Granite, Stony Lake	*d*	63·9	4963	78	4·06	17580	4330	3·20	8212	2566
Granite, Querigut	*d*	70·7	6129	87	4·26	17828	4185	2·60	6625	2548
1/1 K1921/St. L.	*d*	56·7	4222	74	2·29	10200	4454	7·11	17402	2448
1/1 Q/C	*d*	60·1	4810	80	2·39	10545	4412	6·30	15070	2392
Argillaceous Limestone 1a	*e*	21·5†	1503	70	1·07†	5483	5124	41·3	127307	3984
Refractory 76	*e*	54·7	3842	70	1·54	6478	4206	0·27	1115	4130
Refractory 77	*e*	32·4	1900	59	2·10	8180	3895	0·26	1042	4008
Refractory 78	*e*	20·7	1483	72	2·83	11731	4145	0·38	1196	3147
Magnesite 104	*e*	2·5	250	100	0·01	514	5140	—	—	—
Glass 91	*e*	67·5	5487	81	3·30	13891	4209	10·5	24960	2377
Clay 98	*e*	64·2*	5214	81	3·44*	15581	4529	0·21	1042	4962
1/1 91/98	*e*	65·8*	5410	82	3·37*	14925	4429	5·36	12804	2389
1/3 91/98	*e*	—	—	—	—	—	—	2·79	6887	2468
3/1 91/98	*e*	—	—	—	—	—	—	7·93	18663	2353
SiO_2 (Specpure)	—	100	9966	100	(0)	395	—	(0)	574	—

* After ignition at 600° C.
† After ignition at 950° C.
a. Geological Survey and Museum, London; analyses quoted from "Chemical Analyses of Igneous Rocks, Metamorphic Rocks and Minerals," Geological Survey, London, 1931.
b. Geological Survey and Museum, London; analyses quoted from "Mineral Resources 34: Rock Wool," Geological Survey, London, 2nd Edition, 1949.
c. Geological Survey and Museum, London; analyses have not been published.
d. Department of Mineralogy and Petrology, University of Cambridge.
e. U.S. Bureau of Standards.

than 4 to 5 per cent.) and standard curves derived from rocks of low water and organic-matter content, it is preferable, for determinations of silica and potassium oxide, to use discs of ignited rock, the determined compositions from the calibration curves being re-calculated to an air-dry basis, on the basis of the determined loss on ignition. This is because of the increased matrix effect of a substitution of O, H and C for the dominant Si and Al of rock powder, which occurs with light elements. For calcium and heavier elements, the effect of this matrix difference is only significant if there are extremely high contents of water, organic matter, or CO_2 in limestones. Such an effect is seen in Table II. The results for iron in artificial mixture show the fall in X-ray count when C, H and O (as cellulose) are substituted for silica and the reduction of this effect brought about by the bismuth oxide additive. In the general analysis of igneous rocks and non-argillaceous sediments, the samples for all elements determined here are of air-dry rocks. In limestone analysis, it would be preferable to use a separate set of calibration curves from those used for general silicate rocks. It is emphasised that the counts given in Table IV are, except for silica, single 30-second counts. Improved accuracy, especially for low count-rates, *e.g.*, for low contents of calcium, can be obtained by longer counts.

It is clear that if a graph of the results in Table IV were plotted, the results for silica would show the greatest deviations from a calibration curve, partly because of the greater effect of the factors of particle size discussed earlier. Otherwise, the plotted results show

TABLE IV—*continued*

Sample	TiO_2			MnO			Total iron as Fe_2O_3		
	percentage content	X-ray count	ratio of X-ray count to percentage content	percentage content	X-ray count	ratio of X-ray count to percentage content	percentage content	X-ray count	ratio of X-ray count to percentage content
Rhyolite 708	0·26	6182	23777	0·11	2177	19791	1·50	6411	4274
Rhyolite 169	0·19	5054	26600	0·09	1662	18467	3·43	14126	4118
Shale 1056	0·79	15003	18991	0·01	1511	151100	5·55	23646	4260
Calcareous Shale 1424	0·34	7115	20926	0·13	2680	20615	3·45	12670	3672
Calcareous Shale 1425	0·72	16572	23017	0·11	2638	23982	3·94	17453	4430
Dolerite, Carnmoney	2·10	34567	16460	0·19	6031	31742	12·59	41578	3302
Basalt, Kilauea 1921	2·85	41931	14712	0·18	5396	29978	12·40	40217	3243
Basalt, Kilauea 1960	2·68	36856	23269	0·18	5456	30311	12·87	39132	3041
Granite, Stony Lake	1·21	20250	16736	0·11	4162	37836	6·88	24268	3527
Granite, Querigut	0·30	7241	24137	0·03	1960	65333	2·44	9387	3847
1/1 K1921/St. L.	2·03	32008	15767	0·15	4857	32380	9·64	32651	3387
1/1 Q/C	1·20	20848	17373	0·11	4096	37236	7·52	26426	3514
Argillaceous Limestone 1a	0·16	3949	24681	0·04	2055	51375	1·60	5437	3398
Refractory 76	2·21	41662	18852	0·02	1552	77600	2·38	9843	4136
Refractory 77	2·93	57513	19629	0·01	1102	110200	0·90	4076	4529
Refractory 78	3·37	62569	18566	0·005	1068	213600	0·79	3597	4553
Magnesite 104	0·03	2003	66767	0·4	14108	35270	7·07	28267	3998
Glass 91	0·02	1792	89600	—	1075	—	0·08	652	8150
Clay 98	1·4	29520	21086	0·005	1192	238400	2·10	9125	4345
1/1 91/98	0·71	15954	22470	—	1190	—	1·09	4815	4417
1/3 91/98	1·06	22590	21311	—	—	—	1·60	7115	4447
3/1 91/98	0·36	8510	23639	—	—	—	0·58	2714	—
SiO_2 (Specpure)	—	—	—	(0)	981	—	(0)	460	—

good correlation between chemical analysis and X-ray count, with the exception of group deviations for titanium dioxide and manganese oxide, which perhaps result from the chemical data rather than the X-ray method.

TEST OF METHOD—

In routine procedure, a working curve is set up for each element by using about five analysed standards selected from the calibration material quoted in Table IV. A batch of samples is then analysed against this calibration under standard operating conditions, chosen to be optimum for each element as indicated in outline in Table III. As a test of the preparation and analysis procedure, analyses have been made of silica, potassium oxide, calcium oxide, titanium dioxide, manganese oxide and total iron as Fe_2O_3, in the standard[18] granite G–1, diabase W–1 and a 1-to-1 mixture of G–1 and W–1. These rocks were supplied as powders that passed a 300-mesh sieve, but otherwise were subjected to the routine preparation and analysis procedure previously described. Table V gives the general range and extreme single values of contents of the relevant elements as determined by 34 analysts in the co-operative investigation[18] of these rocks, and three replicate values of the content determined by this X-ray spectrographic method. Further development[19] of the co-operative investigation by other analysts provided "recommended values" (see Table 17 of Geological Survey Bulletin 1113 [19]) for composition of G–1 and W–1 that differ slightly from the arithmetic means of the earlier work, and these are quoted in Table V. The results show that silica is least accurately determined by the method, but that for most other elements and replicate determinations, values obtained fall within the suggested limits of acceptability. This is not so for calcium oxide in sample disc 1 of W–1, and total iron as Fe_2O_3 in sample disc 2 of W–1. The similarly high and low values, respectively, for G–1 to W–1 mixture for the two corresponding discs, however, suggest that it is possible that the values determined by the X-ray spectrograph do represent real differences between the material for these two discs, which were obtained in separate batches from the United States Geological Survey. A more likely suggestion is, perhaps, that there is a difference in the particle size of the two samples of W–1, but no evidence has been obtained for this.

TABLE V

TEST ANALYSES OF G–1, W–1 AND A 1-TO-1 MIXTURE OF G–1 AND W–1

	G–1					W–1					1-to-1 mixture of G–1 and W–1			
			Values† determined by X-ray spectrography, per cent.					Values† determined by X-ray spectrography, per cent.						
Oxide	Range of content* in co-operative investigation, per cent.	Recommended values and acceptability limits,[19] per cent.	(*i*)	(*ii*)	(*iii*)	Range of content* in co-operative investigation, per cent.	Recommended values and acceptability limits,[19] per cent.	(*i*)	(*ii*)	(*iii*)	Recommended values and acceptability limits from means of G–1 + W–1,[19] per cent.	(*i*)	(*ii*)	(*iii*)
SiO_2	(71·05) 71·54 to 72·74	72·65 (71·87 to 72·83)	73	72	72	51·28 to 53·01	52·64 (52·07 to 52·73)	53	53·5	49·5	62·64 (61·97 to 62·78)	67	66·5	63·5
K_2O	(3·85) 5·30 to 5·84 (6·88)	5·43 (5·03 to 5·81)	5·4	5·4	5·05	(0·41) 0·57 to 0·82 (1·30)	0·64 (0·54 to 0·80)	0·75	0·70	0·70	3·04 (2·79 to 3·31)	3·1	3·2	3·1
CaO	1·16 to 1·60 (1·90)	1·36 (1·28 to 1·52)	1·44	1·45	1·40	10·55 to 11·42	10·94 (10·81 to 11·13)	11·95	11·70	11·05	6·15 (6·05 to 6·33)	6·4	6·5	6·1
TiO_2	0·16 to 0·35 (0·50)	0·24 (0·22 to 0·30)	0·26	0·28	0·25	(0·10) 0·91 to 1·41	1·08 (0·87 to 1·27)	0·93	1·02	0·96	0·66 (0·55 to 0·79)	0·60	0·66	0·60
MnO	(0·01) 0·02 to 0·04 (0·06)	0·027 (0·02 to 0·04)	0·026	0·027	0·025	0·10 to 0·26 (0·53)	0·18 (0·12 to 0·22)	0·176	0·175	0·167	0·104 (0·07 to 0·13)	0·106	0·12	0·097
Total iron as Fe_2O_3	(1·29) 1·85 to 2·5 (2·99)	1·96 (1·76 to 2·32)	1·95	2·02	1·8	10·7 to 12·18	11·10 (10·94 to 11·50)	11·5	11·4	10·7	6·53 (6·35 to 6·91)	6·55	6·60	6·20

* The general analytical range and extreme single values (in brackets) are indicated by extracts from the full data given by Fairbairn *et al.*[18]

† Values in groups (*i*) and (*ii*) are for analyses of the same sample disc on separate occasions, and in group (*iii*) are for analyses of a different sample disc made from a second supply of material.

Discussion

It is not suggested that such results by X-ray fluorescence spectrography are as accurate as can be obtained by other X-ray spectrographic procedures, but they indicate that quite rapid and acceptable analyses are possible for several important rock elements in material of varied lithology without extensive sample preparation. In many studies, large numbers of samples require to be analysed for some or all of these elements, but complete rock analysis is not required. Where complete analysis is required, the method may still be usefully used for determining some elements either as the sole technique or as a rapid check on conventional analysis. Other heavy elements can be determined in this way by using similar instrumental conditions. The use of a chromium-target tube improves the fluorescent yield from light elements. For phosphorus in rocks of high phosphate content, this may be helpful to the use of the powder method, but, for magnesium and aluminium, particle-size and matrix effects probably prevent accurate quantitative analysis. It seems that fusion methods of sample preparation are essential for accurate determination of these elements. Trace elements, except where present in greater than normal amounts, *e.g.*, for zinc and nickel in some rocks, probably require concentration techniques, and have most often been determined elsewhere by numerical comparison of counts obtained against single standards of similar matrix, rather than from standard curves. Analysis for major heavy elements in minerals, *e.g.*, ores, should be convenient and simple by this powder-disc technique, provided that large changes in matrix are avoided for a single calibration curve. From the stage, essential to all analytical techniques, at which the rock has been reduced to a fine powder, it appears that with one worker, 100 samples can reasonably be mixed and pelleted in 13 hours, the analysis for six elements in these 100 samples occupying about a further 24 hours, *i.e.*, a total of about 5 man-days.

I am grateful for helpful discussions with Dr. D. F. Perkins during the course of this work and for assistance and much valued advice on instrumental matters from Mr. G. H. Owen. The Nature Conservancy thanks The United States Geological Survey for samples of G–1 and W–1, Dr. S. O. Agrell, Department of Mineralogy and Petrology, University of Cambridge, for supplying rocks analysed by Mr. J. H. Scoon, and the Geological Survey of Great Britain for providing, through Dr. P. A. Sabine, analysed rocks. I thank Dr. B. M. Kaye of the Whiting and Industrial Powders Research Council (then the Research Council of the British Whiting Federation) who kindly provided the sized samples of pure limestone and precipitated calcium carbonate.

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An Improved Method of Pyrolysis in Gas Chromatography

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An improved method of pyrolysis is described for the quantitative micro-analysis of non-volatile compounds by gas - liquid chromatography. The sample is pyrolysed in the glass capillary in which it is weighed. With up to 30 μg of sample an accuracy of at least ±5 per cent. can be achieved.

The equipment used consists of an Oertling Q01 quartz-fibre microbalance and a Pye Panchromatograph fitted with a Pye pyrolysis unit and a flame ionisation detector, modified for use with radioactively labelled compounds.

THE technique of pyrolysis and gas chromatography as described by Janák[1,2] has been modified and applied to the examination of non-volatile radioactively labelled compounds.

The published methods of pyrolysis have been reviewed by Perry.[3] Many of these methods involve the pyrolysis of relatively large, solid "injections," or lumps of material, weighing from 1 to 50 mg, by heating in devices consisting of large coil filaments or tube furnaces connected in line with the carrier-gas stream of the chromatograph. Alternative methods involve heating the samples in sealed tubes, which are then opened in the carrier gas. Such devices suffer from the disadvantages that the geometries of the larger samples are difficult to reproduce and the rate of heating and final temperature are critical. Also, the pyrolysis products are usually well diluted with carrier gas before entering the gas-chromatograph column and do not arrive at the packing as concentrated "plugs," which results in broadening of peaks with a corresponding loss of resolution. Nevertheless, qualitative results of value have been obtained and also some quantitative results, particularly for polymers.

The coil-filament and furnace techniques have been compared by Perry, and the advantages of both are retained in the capillary method described in this paper. It was developed after difficulties were encountered in the use of the Janák technique as recommended for the Pye pyrolysis unit.

Experimental

At first, attempts were made to reproduce the results obtained by Janák.

Samples of atropine (50 to 90 μg) in ethanol solution were dispensed on to the Pye coil from a weight pipette. The ethanol was either allowed to evaporate spontaneously or dried by gentle heat from an electric light bulb, before the residue was pyrolysed in the chromatograph column.

Although the pyrolysis patterns, or "pyrograms," obtained were qualitatively reproducible, the ratio of peak heights or areas to sample weight varied widely.

The effect of pyrolysing samples in glass capillaries, sealed at one end and placed inside the Pye coil with the open end uppermost, was tried, the capillary and sample being weighed on an Oertling quartz-fibre microbalance. This technique was very sensitive, gave "pyrograms" of excellent quantitative reproducibility and showed that the atropine used for testing the Janák method was homogeneous.

Method

Apparatus—

The capillaries—Prepare the capillaries by drawing down 1·7- to 1·9-mm outer diameter, 1·1- to 1·3-mm inner diameter, glass tubing to 0·5-mm outer diameter. Seal off a short piece, avoiding the formation of a blob of glass, and snap it to a length of 2 mm.

The capillary should be an easy fit inside the pyrolyser coil with the open end just clear of the top turn (see Fig. 1).

Weighing stands—During weighing, support the capillaries vertically in a hole pierced in a "chair-shaped" stand prepared from a 4 × 16-mm rectangle of 0·065-mm aluminium foil; use an identical stand and capillary as a counterpoise.

Capillary filler—Use a glass funnel, 3 to 4-cm long with an 0·5-mm outer diameter stem as a filler. Attach the capillaries to the stem tip by a polythene connector 2 mm long.

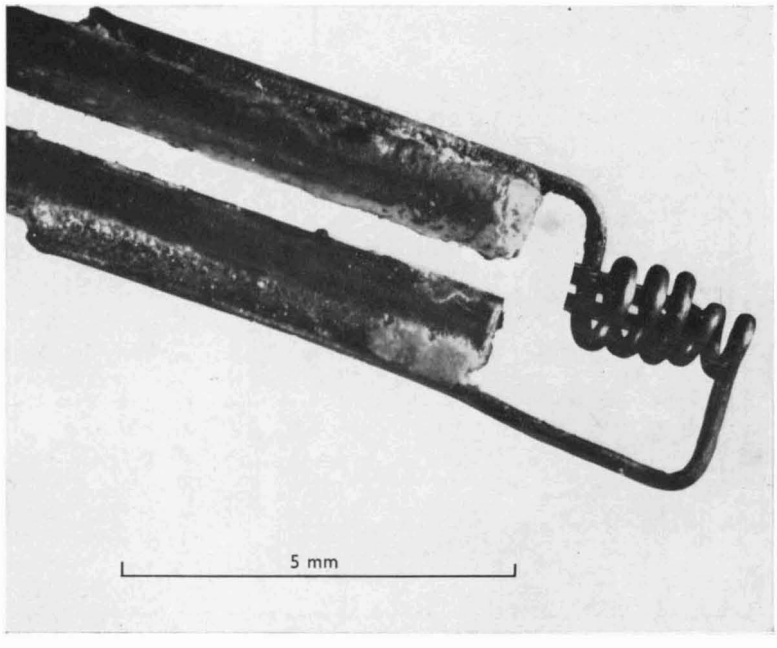

Fig. 1. Capillary fitted inside pyrolyser coil

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MODIFICATIONS TO THE PYE PYROLYSER AND PANCHROMATOGRAPH—

The pyrolyser—The device follows the design of Parriss and Holland[4] and consists of a 5-turn nichrome coil mounted on the tips of tungsten support wires, which are sealed through a B7 cone to fit the column inlet. The top of the cone is provided with a side arm as a carrier-gas inlet. Carrier gas also enters the column through a pre-heater limb. It is advantageous to replace the side-arm inlet by a "bleed" tap for the slow release of the carrier-gas pressure, thus permitting the column inlet to be opened to the atmosphere without the gas-supply controls being touched. A B7 cone and "bleed" tap is used to stopper the column inlet between pyrolysis runs. All joints are secured by hooks and spring clips.

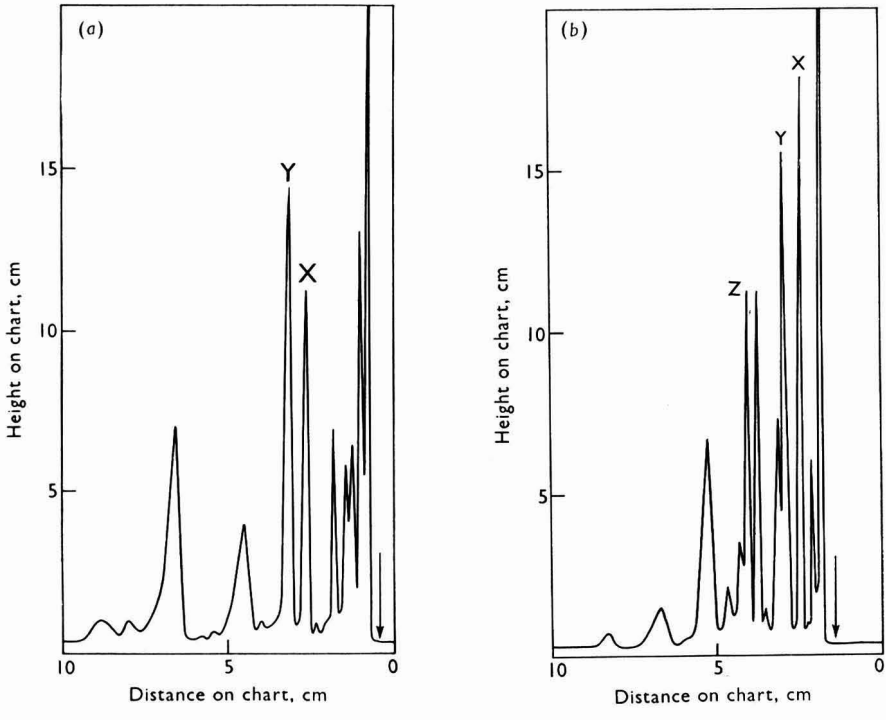

Fig. 2. "Pyrograms" obtained for (*a*) 20·0 μg of atropine and (*b*) 10·4 μg of bilirubin

The flame ionisation detector—The detector has a cylindrical metal body fitted with a push-on lid, waste gases being normally discharged to atmosphere through a gap round a side terminal. For the analysis of radioactively labelled compounds the detector is modified so that radioactive gases are diverted through a curved brass spout soldered to a hole drilled in the lid of the detector, the terminal gap in the detector body being sealed by a polytetrafluoroethylene washer. A loosely fitting metal tube is slipped over the spout and connected to a trap and coarse vacuum pump so that a Venturi draught is maintained round the mouth of the spout. This modification does not affect the response of the detector.

The carrier-gas flow-rate may be accurately measured, while the column is hot, by removing the detector lid and connecting the jet to one of the soap-film meters by means of a polyvinyl chloride tube fitted with a polytetrafluoroethylene nozzle. The polytetrafluoroethylene does not leave traces of interfering material on the jet, as does polyvinyl chloride.

PROCEDURE—

Sample dispensing—After wiping and weighing the capillary, attach it to the filler and tap in dry, finely powdered sample until the capillary is not more than one-third full.

Detach the capillary and before re-weighing clean it on the outside with a sable brush

and compact the sample by holding the capillary in forceps and tapping the forceps on a hard edge.

Dispense non-volatile viscous liquids into the capillary on the top of a fine wire.

The pyrolysis—Divert the carrier gas to the atmosphere by the B7 cone and tap, and then replace the cone and tap by the pyrolyser unit.

When the flow-rate of the carrier gas has returned to the initial value, pyrolyse the sample for 10 seconds.

After the analysis, open the pyrolyser "bleed" tap and replace the unit by the B7 cone.

Results

Samples (5 to 30 μg) of various substances, including atropine, haemin, bilirubin, vitamin A, n- and isoleucine, vitamin B_{12} and *p*-chloromercuribenzoic acid, have been pyrolysed. Figs. 2 (*a*) and (*b*) show "pyrograms" obtained for pure atropine and bilirubin, respectively. The graphs obtained by plotting weight of sample against heights or areas of selected peaks were linear in the range 5 to 30 μg of sample, as can be seen in Figs. 3 (*a*) and (*b*), which give graphs plotted from values obtained for peaks in Figs. 2 (*a*) and (*b*), respectively.

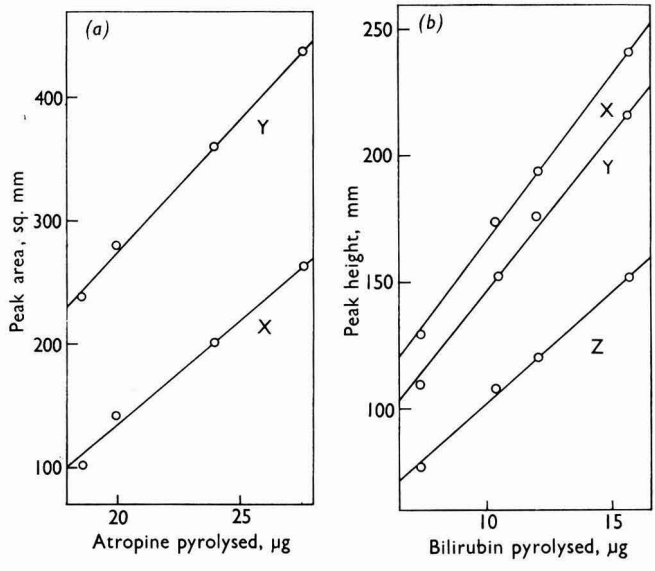

Fig. 3. Graphs obtained (*a*) by plotting amount of atropine pyrolysed against peak area for peaks labelled X and Y in Fig. 2 (*a*), and (*b*) by plotting amount of bilirubin pyrolysed against peak heights for peaks X, Y and Z in Fig. 2(*b*)

The purity of radioactively labelled compounds has been determined by comparisons with pure inactive compounds.

CHROMATOGRAPH CONDITIONS—

	Atropine	Bilirubin
Pyrolysis temperature (for 10 seconds) ..	600° C (medium)	400° C (low)
Column	5-foot Apiezon L	5-foot Apiezon L
Column temperature	80° C	125° C
Flow-rate of carrier gas (nitrogen) ..	90 ml per minute	90 ml per minute
Chart speed	20 inches per hour	10 inches per hour
Amplifier range	10^{-10}	10^{-10}

Discussion

The lack of reproducibility in the initial experiments, in which atropine was pyrolysed directly on the coil, may have been due to uneven deposition from the solvent or deposition on parts of the coil that did not attain the required temperature for pyrolysis.

The results obtained by the capillary technique were so satisfactory that no further experiments on direct deposition on the coil were made.

The following observations by Janák on micro-pyrolyses have been confirmed by using the capillary technique—

(*i*) The reproducibility of pyrolyses involving very small samples (micrograms) depends on a constant and adequate flow-rate of carrier gas and not on the final temperature or rate of heating, provided that the temperature is above that at which pyrolysis occurs.

(*ii*) The constant geometry of such small sources ensures uniform heating.

(*iii*) The duration of heating is important and must be long enough (10 seconds) to ensure that pyrolytic fission has been as complete as possible.

SUMMARY OF ADVANTAGES OF PYROLYSING IN A CAPILLARY—

(*a*) The need for a volatile solvent is eliminated; many non-volatile materials are insoluble or are not soluble enough for satisfactory dispensing in solution. Traces of solvents can also remain with the sample and interfere with the pyrolysis.

(*b*) The geometry of the pyrolysis source is reproducible and samples are subjected to a uniform heating.

(*c*) The capillary retains any pyrolysis residues, which might fall off the coil after direct deposition and contaminate the column packing.

(*d*) The capillaries used are small and shallow enough for the volatile radicals and compounds produced in pyrolysis to escape quickly and be swept away in the carrier-gas stream and so prevent secondary reactions with the residue.

(*e*) Pyrolysis still occurs close to the column packing where the products are not excessively diluted with carrier gas.

(*f*) The coil is protected from the attack by carbon, noted by Perry and investigated by Jennings and Dimick[5]; a long life and constant electrical resistance for the coil is thus ensured.

(*g*) Within the ranges of sample size tested, excellent reproducibility and linearity can be achieved.

I thank Mr. D. A. Lambie for his interest and encouragement in this work.

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The Absorptiometric Determination of Silicon in Water

Part V.* Continuous Automatic Determination of "Reactive"† Silicon

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The use of the Technicon AutoAnalyzer for the continuous, automatic determination of "reactive" silicon in water has been studied. The instrument performed very reliably, and appears to be suitable for the continuous analysis of waters in power stations.

The determination of silicon in water samples from the steam-water circuit of power stations is of great importance for high-pressure units. Previous papers[1,2,3,4] have described manual methods for this determination. The use of automatic rather than manual analytical techniques can produce several well known benefits. Accordingly, a study has been made of the automatic determination of "reactive" silicon in water; the results are given in this paper.

A commercially available instrument, the Technicon AutoAnalyzer, was chosen for this work for several reasons. Firstly, it can be used for the continuous analysis of a plant-stream. Secondly, the instrument can be readily converted from one determination to another, and this would be advantageous in power stations. Finally, the successful use of the instrument in power stations had been reported by several workers,[5,6,7,8,9] although few detailed quantitative results were quoted. The AutoAnalyzer was conceived by Skeggs,[10] and its principles and mechanisms have been discussed by Ferrari, Russo-Alesi and Kelly[11]; essentially, the instrument provides a means of making absorptiometric analyses automatically.

Experimental

Apparatus—

AutoAnalyzer components—The proportioning-pump and chart-recorder were standard items. The recorder was fitted with a range-expansion unit so that the chart-width could be made to correspond to transmission ranges of 0 to 100, 50 to 100, 75 to 100, or 90 to 100 per cent. The colorimeter was a standard model, except that it contained red-sensitive photocells so that measurements could be made close to the absorption peak (810 mμ) of reduced β-molybdosilicic acid. Interference filters were used to isolate the required wavelength; their peak transmission was at 814 mμ, and their half-band width was about 14 mμ. Red-glass filters were used to eliminate other transmission bands of the interference filters. The flow-cell in the colorimeter was of the standard, continuous-overflow type, and had an optical path length of 1·5 cm. Flow-cells with a small hold-up volume are preferable, but were not available when this investigation was made. All glass coils, tubing, and glass connections were standard items; Tygon pump tubing was used throughout.

Choice of reaction system—The term "reaction system" is used here to denote the assembly of tubing, glass coils, etc. (from the proportioning-pump to the colorimeter), used to achieve the formation of the desired coloured product. Previous papers in this series[2,4] have shown that the method in Part IV[4] is suitable for determining "reactive" silicon in all samples from the steam-water circuit of power stations. Accordingly, this method was adapted to the AutoAnalyzer; the final coloured product is a reduced β-molybdosilicic acid, and the reactions involved in its formation and reduction are discussed in Part I.[1]

A diagrammatic representation of the reaction system is shown in Fig. 1. The rates at which sample and reagents were pumped into the system were chosen so that the concentration of each reagent in the solution emerging from the reaction system was the same as that in the final solution of the manual method. Because of the sizes of tubing available for the proportioning pump, the concentration of each reagent solution had to be changed from those in the manual method. Each reagent was prepared as described under "Reagents."

* For details of earlier parts of this series, see reference list, p. 277.

† "Reactive" silicon has been defined in previous parts of this series as those forms of silicon, mainly monomeric and dimeric silicic acid, that react with ammonium molybdate in 10 minutes under the conditions of the method given in Part II. This definition is retained in this part for simplicity, but, because of the shorter reaction time used with the AutoAnalyzer, dimeric silicic acid will probably not be quantitatively determined.

In designing the reaction system, allowance had to be made for the times required for the different chemical reactions to occur. However, there are two conflicting requirements for these times. Short reaction times are desirable to decrease the time lag in the response to changes of concentration, but if the times are too short to allow the reactions to go to completion, sensitivity is lost, and the precision and robustness of the system may suffer. An investigation was made of the effect of variations in reaction times, and on this basis, the reaction times indicated in Fig. 1 were selected. Tests showed that, in the absence of orthophosphate, about 95 per cent. of the monomeric silicic acid in a sample was converted to reduced β-molybdosilicic acid at 20° C. The presence of 50 p.p.m. of orthophosphate in the sample decreased the rate of formation of β-molybdosilicic acid. Therefore for samples containing orthophosphate, the first delay coil was made equivalent to $4\frac{1}{2}$ minutes.

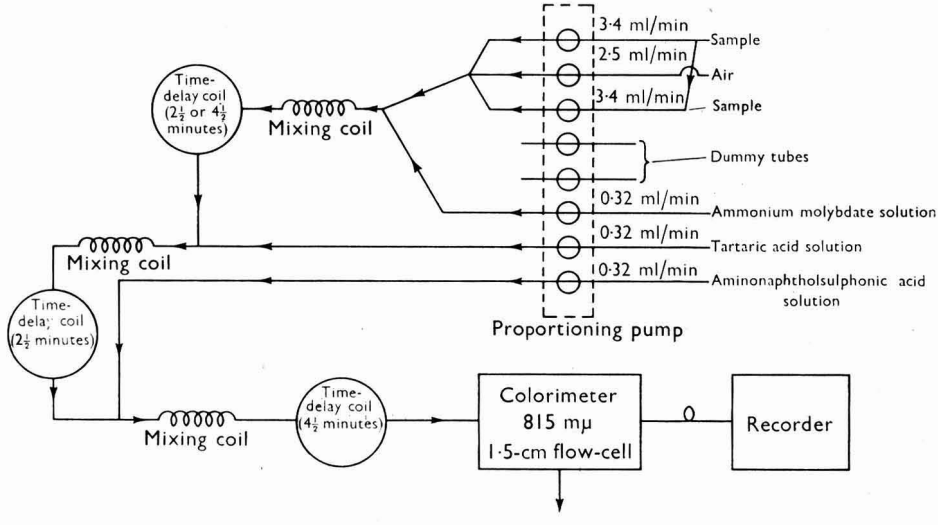

Fig. 1. Reaction system for the AutoAnalyzer

When it was required to change the concentration of silicon in the solution being analysed, this was done manually by lifting the sample tube from one solution, washing the outside of the tube with water, drying it with filter-paper, and then placing it in the second solution. This technique tended to cause rather greater fluctuations than normal in the response of the recorder. This disturbance persisted only for the few seconds, corresponding to the time when the sample tube was not immersed in a solution, but was otherwise without effect.

REAGENTS—

Analytical-grade reagents were used whenever possible, and distilled water was used throughout. All solutions were stored in polythene bottles. Standard solutions of sodium silicate were prepared as described previously[2]; other solutions of required silicon concentrations were prepared by diluting the stock solution with water. The three reagent solutions were prepared as described below. Four litres of each reagent were usually prepared, and this volume was sufficient for about 200 hours continuous operation. During the work, the temperature of the laboratory varied between 18° and 25° C.

Ammonium molybdate - sulphuric acid solution—An ammonium molybdate solution was prepared by dissolving 216 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.H_2O$, in about 3 litres of water. A 152-ml volume of 98 per cent. sulphuric acid was added to about 800 ml of water, the solution was then cooled, and added to the molybdate solution with stirring. This solution was then diluted to 4 litres with water.

Tartaric acid solution—This was prepared by dissolving 740 g of tartaric acid in water and diluting the solition to 4 litres.

1-*Amino*-2-*naphthol*-4-*sulphonic acid solution*—A solution of sodium sulphite was prepared by dissolving 45·2 g of sodium sulphite, $Na_2SO_3.6H_2O$, in about 400 ml of water, and in this solution were dissolved 3·8 g of 1-amino-2-naphthol-4-sulphonic acid. The solution was then diluted with water to about 3·5 litres, and 264 g of potassium metabisulphite, $K_2S_2O_5$, dissolved in the solution, which was then diluted with water to 4 litres. Care was required to ensure complete dissolution of all the materials before this reagent was used. Otherwise, undissolved material tended to deposit within the tubing of the reaction system, and cause partial blockage.

Results

Response time—

The time elapsing between a change in the silicon concentration of a sample and the first detectable response to this change was either 10 or 12 minutes, depending on the length of the first time-delay coil in the reaction system. This lag corresponds to the time taken by the solution to flow through the system and reach the flow-cell of the colorimeter. Once the first response occurred, the response of the recorder rapidly approached its new equilibrium value; typical recorder traces are shown in Figs. 2 and 3. To check the time required for one solution completely to displace an earlier solution in the flow-cell, distilled water was analysed alternately with solutions containing different concentrations of silicon. In the range 0·01 to 2 p.p.m. of silica, the recorder indicated 50, 90 and 99·5 per cent. of the final response at times of 0·5, 1 and 6 minutes, respectively, after the first detectable response.

Other tests, in which the silicon concentration in the sample was changed for only 1 or 2 minutes, showed that the response to such pulses was predictable from the rates of response given above.

Calibration curve and precision—

Solutions containing different concentrations of silicon were analysed alternately with distilled water, each solution being allowed to run for 15 minutes to ensure that the equilibrium response of the recorder was attained. The response to the distilled water was adjusted whenever necessary to correspond to a transmission of 100 per cent. Depending on the concentration of silicon in the samples, the range-expansion unit was adjusted so that the scale of the recorder corresponded to transmissions of either 0 to 100 or 90 to 100 per cent. Tests made with the first of these ranges lasted for 3 days, whereas 2 days were taken for tests with the other range; during this time each concentration of silicon was analysed several times. The equilibrium readings of the recorder were noted for each solution, and then converted to optical-density units; a summary of all the results is given in Table I.

Table I

Calibration curve and precision of the AutoAnalyzer

Silicon in sample, p.p.m. of silica	Optical density	Number of determinations	Standard deviation, p.p.m. of silica	Coefficient of variation, per cent.
Transmission range, 0 to 100 per cent.—				
5·00	1·490	2	—	—
2·00	0·785	3	—	—
1·00	0·397	14	0·0060	0·6
0·50	0·199	15	0·0050	1·0
0·20	0·079	16	0·0028	1·4
0·10	0·040	16	0·0023	2·3
Transmission range, 90 to 100 per cent.—				
0·100	0·0390	9	0·0008	0·8
0·050	0·0193	8	0·0007	1·4
0·010	0·0035	9	0·0003	3·0
0·005	0·0017	10	0·0009	18·0

Table I shows that the calibration curve was linear to within 1 per cent. for concentrations of less than 2·0 p.p.m. of silica when the range of the recorder corresponding to transmissions of 0 to 100 per cent. was used. When the 90 to 100 per cent. range was used, results for solutions containing 0·1 and 0·05 p.p.m. of silica agreed well with those expected from the results on the other range, but the results for 0·01 and 0·005 p.p.m. of silica were slightly lower than expected. The maximum discrepancy was equivalent to only 0·001 p.p.m. of

silica, and errors involved in reading the chart may account for much of this. Manual tests with the same reagents and solutions showed that the optical density obtained with the AutoAnalyzer was about 87 per cent. of that for measurements made manually at the absorption peak with a spectrophotometer. Slightly incomplete formation and reduction of the β-molybdosilicic acid, and the use of filters rather than measuring at the absorption peak probably account for the smaller sensitivity of the AutoAnalyzer.

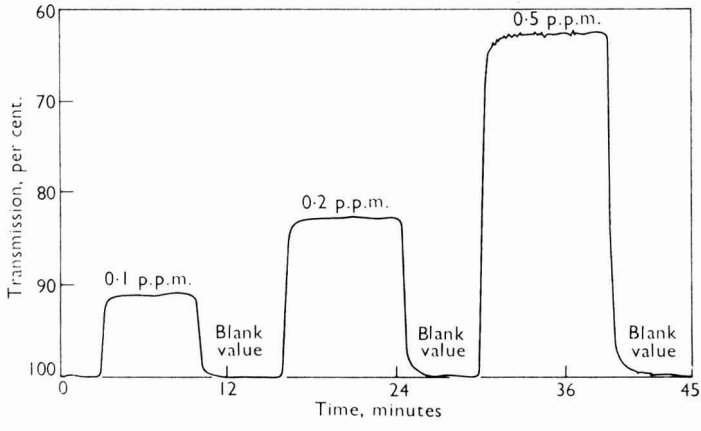

Fig. 2. Recorder traces for solutions containing 0·1 to 0·5 p.p.m. of silica

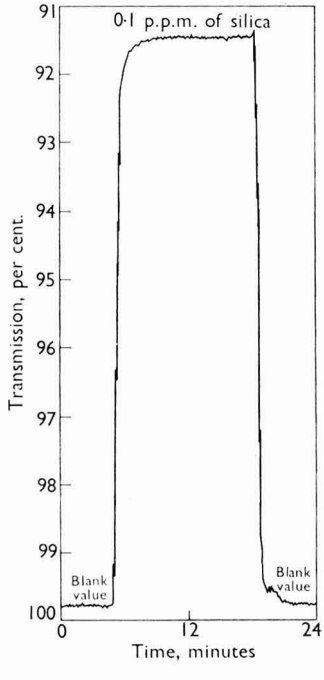

Fig. 3. Recorder trace for a solution containing 0·1 p.p.m. of silica (expanded recorder scale)

Table I also shows that the response of the system may be calibrated precisely with solutions containing eiher 1 or 0·1 p.p.m. of silica, depending on the transmission range

STABILITY OF THE REPONSE—

When the AutoAnalyzer is used for continuous analysis, it is desirable that its response to a given concentration of silicon should not vary markedly with time. The response will remain constant provided that—

(*a*) the slope of the calibration curve remains constant;

(*b*) the response equivalent to the reagent blank value remains constant.

Although the response of the AutoAnalyzer may be automatically standardised at pre-set intervals, factors (*a*) and (*b*) were investigated to obtain an estimate of the basic stability of the system.

Stability of the calibration curve—The stability of the calibration curve over a few days of discontinuous use has already been indicated by the results in Table I. The stability over longer periods was checked in two sets of experiments.

In the first set, the AutoAnalyzer was run continuously for 300 hours. Fresh reagents and pump-tubing were prepared, and used for the whole of this run. Distilled water was analysed throughout except on twelve occasions (distributed evenly over the period) when the system was calibrated with a solution containing 0·1 p.p.m. of silica. The range of the recorder corresponded to transmissions of 90 to 100 per cent., and the only adjustment made throughout this period was to set the response to distilled water to 100 per cent. just before each calibration. The coefficient of variation of the twelve results was 0·9 per cent.; this precision is not significantly different from that obtained over shorter periods of time (see Table I). The results indicate that ageing of reagents and pump-tubing, and long-term variations in the response of the colorimeter and recorder had negligible effects on the slope of the calibration curve over the period of 300 hours.

In the second set of tests, the AutoAnalyzer was used discontinuously over a period of 6 months during which time many different batches of reagents were used, and several changes of pump-tubing were made. During this time, the AutoAnalyzer was often calibrated (transmission range 0 to 100 per cent.) with a solution containing 1·5 p.p.m. of silica. The coefficient of variation of 62 such calibrations was 0·85 per cent., which confirms the good stability of the calibration curve.

Stability of the response to the reagent blank solution—Distilled water was analysed continuously for periods of about 20 hours, and in one experiment for 76 hours; no adjustment was made to the AutoAnalyzer during each experiment. The range of the recorder corresponded to transmissions of 90 to 100 per cent., and after each run the maximum and minimum readings were noted. For nine such experiments of 20 hours' duration, the average difference between these two readings was equivalent to 0·002 p.p.m. of silica, with a standard deviation of 0·001 p.p.m. of silica. The difference between the two readings for the 76-hour run was equivalent to 0·007 p.p.m. of silica. The causes of these long-term variations were not investigated, since the response was considered adequately stable for applications in power stations. However, it is thought that the variations were largely caused by instability of the colorimeter and recorder.

The charts from these tests were also analysed to obtain a measure of the short-term stability of the system. For this purpose, the maximum and minimum readings in 280 30-minute periods were noted. The average difference between these two readings was equivalent to 0·0003 p.p.m. of silica with a standard deviation of 0·0001 p.p.m. of silica. The short-term stability was therefore such that very small changes in concentration could be rapidly observed for concentrations close to zero.

Effect of continued analysis of solutions containing silicon—Solutions containing 1·0, 0·2 and 0·1 p.p.m. of silica were analysed continuously for periods of 16 hours with the recorder covering the transmission range 0 to 100 per cent. The average differences between the maximum and minimum readings in 30-minute periods were equivalent to less than 0·003, 0·0015 and 0·001 p.p.m. of silica, respectively. These limits correspond to the precision with which the chart could be read.

The charts were also analysed to determine the difference between the maximum and minimum readings in each experiment of 16 hours. These differences were equivalent to 0·020, 0·007 and 0·005 p.p.m. of silica for the solutions containing 1·0, 0·2 and 0·1 p.p.m. of silica, respectively. Rather greater differences would be expected from the results in Table I. Accordingly, it is concluded that continued analysis of solutions containing up to 1 p.p.m. of silica has no marked effect on the long-term stability of the system.

EFFECT OF ORTHOPHOSPHATE—

Solutions containing different concentrations of silicon and 50 p.p.m. of orthophosphate (added as disodium hydrogen orthophosphate, Na_2HPO_4) were analysed alternately with distilled water. The longer time-delay coil (equivalent to about $4\frac{1}{2}$ minutes) was used for the first reaction in these experiments, and each solution was analysed for 20 minutes so that the equilibrium response was attained. The recorder range corresponded to transmissions of 0 to 100 per cent., and the equilibrium readings for each solution were noted and converted to optical densities. Each solution was analysed 8 times, and the mean results are given in Table II, which, for comparison, includes results (taken from Table I) in the absence of orthophosphate. In calculating the effect of orthophosphate, allowance was made for the silicon content of the orthophosphate (equivalent to about 0·002 p.p.m. of silica in the solutions analysed); the silicon content was determined as described in Part IV.[4]

TABLE II

EFFECT OF ORTHOPHOSPHATE

Concentration of silicon, p.p.m. of silica	Mean optical density		Effect of orthophosphate, p.p.m. of silica
	0 p.p.m. of orthophosphate	50 p.p.m. of orthophosphate	
0·0	0·000	0·004	0·008
0·1	0·040	0·044	0·008
0·2	0·079	0·083	0·005
0·5	0·199	0·202	0·003
1·0	0·397	0·396	−0·004

The nature of the effect of orthophosphate was similar to that found in Part IV,[4] and that paper should be consulted for a discussion of the effect of orthophosphate. Small differences between the effects in Table II and those reported in Part IV[4] are probably attributable to the different reaction times used for the AutoAnalyzer and the manual method of analysis. The interference was considered adequately small, and no attempt was made to reduce it. These tests also showed that 50 p.p.m. of orthophosphate did not adversely affect the precision and stability of the response.

DISCUSSION

DIFFICULTIES EXPERIENCED—

Preliminary experiments showed that, on continued use, a brown deposit slowly formed at the entrance of the flow-cell. In time, small particles of this deposit detached themselves from the wall and passed into the light-transmitting portion of the flow-cell. These particles had no effect on the average response of the recorder, but caused momentary decreases in transmission when a particle interrupted the light beam. This effect was completely overcome by removing the deposit from the flow-cell by wiping with filter-paper. This operation required only a few minutes, and was normally done once each day. The nature of the deposit was not investigated, but it is thought likely to be aminonaphtholsulphonic acid or one of its oxidation products.

The Tygon pump tubing had to be replaced from time to time. The system was never run continuously until the pump tubing ruptured, but the tests mentioned above showed that new tubing lasted for at least 300 hours; at the end of this time the tubes showed no signs of imminent failure. On one occasion, tap-water was pumped continuously through tubes of four different bores for 5 weeks; at the end of this time tubes with an internal diameter of 0·03 inch split, but greater diameter tubes were still operating satisfactorily. General experience of the system has also confirmed that the smaller-bore tubing tends to rupture more rapidly. Thus, for continuous analysis, it may be more convenient to use larger tubes for additions of reagents, and thus decrease the replacement rate of pump tubing. This would involve some loss of sensitivity because larger volumes of reagents would cause greater diluton of the sample.

RESPONSE TIME—

The time taken to reach the first detectable response to a change in concentration was 10 or 12 minutes depending on the length of the first time-delay coil. Such a delay is adequate for most power-station requirements but could be reduced if required by decreasing the

times allowed for the three chemical reactions involved. For example, for waters containing little or no othophosphate, all three reactions times could probably be halved without markedly affecting the precision and stability of the system. The time for the first detectable response would then be reduced to 5 to 6 minutes.

Once the first response to a new concentration had occurred, a further 6 minutes were required before the equilibrium response was attained. This delay is caused by gradual replacement of the solution in the flow-cell. The more recent design of flow-cell produced by the makers of the AutoAnalyzer considerably reduces the time lag.

PRECISION AND STABILITY—

The results above show that the AutoAnalyzer could be calibrated with good precision, and that the calibration remained essentially constant during prolonged use. The short-term stability, *i.e.*, within 30 minutes, was such that rapid changes in concentration of about 0·001 to 0·01 p.p.m. of silica at concentrations of 0 to 1 p.p.m. of silica, respectively, could be detected. The long-term stability *i.e.*, within a day, was less good, as would be expected. The effect of drift on the ability to detect changes in concentration depends on several factors, *e.g.*, the frequency and precision of calibration, the magnitudes of the drift and concentration change in the sample. A discussion of the interplay of these factors has not been attempted in this paper, but it is concluded that calibration at daily intervals should provide adequate sensitivity for detecting concentration changes of interest in power stations. The sensitivity can obviously be improved by increasing the frequency with which the calibration is checked, and it is simple to arrange that a solution containing a known amount of silicon is automatically analysed at predetermined intervals.

The reasons for the observed drifts were not established, but those observed when distilled water was analysed are probably due to instability in the colorimeter and recorder. Variations in the laboratory temperature were probably an important source of the additional instability found when solutions containing appreciable concentrations of silicon were analysed. The optical density of the reduced β-molybdosilicic acid decreases by about 0·25 per cent. for an increase in temperature of 1° C. Thus for appreciably better stability than that reported in this paper, it is probably desirable to closely control the temperature of the solution in the flow-cell.

APPLICATION OF AUTOANALYZER TO CONTINUOUS MONITORING—

Although the tests described here have dealt with concentrations of less than 2 p.p.m. of silica, samples containing greater concentrations may be simply analysed by using a flow-cell with a smaller optical-path length or by diluting the sample automatically with water. Very few problems of maintenance arose during the use of the AutoAnalyzer, the greatest problem being the need to replace a valve in the amplifier in the recorder. The pump tubing had a limited life, but replacement at fortnightly intervals should be adequate and convenient when the instrument is used for continuous monitoring of a plant stream. The instrument has not been used by the author in a power station, but other workers have reported its successful use under these conditions, and no insuperable problems are foreseen.

The system used in this work makes no allowance for the effects caused by any coloured or suspended materials that may be present in samples. A method of allowing for such effects is described in Part IV.[4] However, this technique requires the optical density of a special blank determination to be subtracted from the optical density of the normal sample determination. This correction could be made automatically by using a colorimeter that holds two flow-cells, and measuring the difference between them. However, the effect may often be decreased sufficiently by suitable dilution of the sample.

It should also be noted that the AutoAnalyzer, as used in this work, does not provide a completely automatic analytical system; some manual analyses are necessary to determine the silicon content of the water used for the reagent-blank setting of the recorder. Without allowance for this silicon content, a bias could arise in future sample analyses. This manual determination may be made as described in Part II.[2]

The spectrophotometric sensitivity[12] for the reduced β-molybdosilicic acid is[1] 0·0026 μg of silica per sq. cm. For comparison, spectrophotometric methods for nickel,[13] iron,[14] copper,[15] hydrazine[16] and ammonia[17] are available with sensitivities of 0·0042, 0·0025, 0·0033, 0·0005 and 0·0028 μg per sq. cm, respectively. Thus, provided errors arising in the reaction system can be adequately controlled, it should be possible to determine these other impurities (of

importance in the chemistry of boiler feed-water) automatically with sensitivities approximately the same as that reported here for silicon. This aspect is now being investigated, and it is hoped to report the results in future papers.

This paper is published by permission of the Central Electricity Generating Board. I thank Mr. C. A. Dawes for experimental assistance, and acknowledge valuable discussions with Mr. I. R. Morrison.

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NOTE—References 1, 2, 3 and 4 are to Parts I, II, III and IV of this series, respectively.

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The Colorimetric Determination of Traces of Lead in Heat-resistant Nickel - Chromium Alloy Steel

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Dibenzyldithiocarbamic acid is used for extracting lead from 0·5 M acid solutions of 25 per cent. nickel - 20 per cent. chromium steel before determination of the lead with dithizone. Three parts per million can be determined with an accuracy of ±1 p.p.m.

The effect of trace concentrations of lead, bismuth and tellurium on the high-temperature creep-rupture and elongation properties of nickel-base alloys has recently been studied.[1] These physical properties were stated to be adversely affected with additions of as little as 5 to 20 p.p.m. of these elements. These findings have been extended to the field of 25 per cent. nickel - 20 per cent. chromium alloy steels and have led to requests for an analytical method for determining lead, covering the range 1 to 20 p.p.m. with an accuracy of ±1 p.p.m. of lead.

A final determination of lead as its dithizone complex would offer the sensitivity required, provided that an initial quantitative separation of lead from interfering elements could be obtained in association with a low lead-reagent blank value.

The direct extraction of traces of lead with dithizone is not applicable to solutions of highly alloyed steels as rapid oxidation of the reagent by iron^{III} occurs in the initially reduced and complexed alkaline cyanide solutions used for extracting lead. Excessive concentrations of citrate are required for complexing chromium and nickel, and these lead to high lead blank values. Existing methods for separating lead involve either precipitation, *e.g.* as sulphide in the presence of a suitable carrier element,[2] lead being subsequently determined by dithizone in the wet-oxidised sulphide residue, or selective removal of all interfering elements, leaving lead in solution. Solvent extraction of iron and volatilisation of chromium as chromyl chloride is typical of the latter method.[3] Our experience has been that both techniques are tedious, involve considerable manipulation with the possibility of extraneous lead contamination, and give high reagent blank values. Blank levels ranged from 20 to 30 μg of lead per g of sample with analytical-grade reagents to 10 to 15 μg for "low-in-lead" reagents.

Neither technique fulfilled the requirements of simplicity and low blank levels necessary for accurate determinations at concentrations of less than 10 p.p.m. of lead.

Experimental

Extraction of lead with diethyldithiocarbamate—

In reports on recent work on the analytical applications of diethyldithiocarbamates, it has been stated that diethylammonium diethyldithiocarbamate could be used for extracting lead[4,5,6,7] from 1·5 M hydrochloric acid solutions without interference from iron^{II}, chromium^{III}, vanadium^{V}, nickel, aluminium, manganese, titanium and zirconium. Experiments were carried out to investigate this procedure.

As no suitable standard steel samples were available, a commercial 25 per cent. nickel-20 per cent. chromium steel stated to contain about 20 p.p.m. of lead (mass-spectrometric determination) was used for the experimental work. Samples (0·25 g) were dissolved in 10 ml of diluted hydrochloric acid (1 + 1) on a hot plate, oxidised with the minimum excess of nitric acid, sp.gr. 1·42, and cooled after nitrous fumes had been boiled off. The solutions were then adjusted to pH 2·0 by adding 50 per cent. ammonia solution and 10 ml of 30 per cent. w/v hydroxylammonium chloride solution. After they had been warmed to reduce iron, the solutions were cooled, diluted to 50 ml with water and transferred to a 100-ml separating funnel; 4 ml of diluted hydrochloric acid were then added to give a final acid concentration of 1 to 1·5 M. Lead was extracted by shaking the solution with 10-ml volumes of diethylammonium diethyldithiocarbamate solution in chloroform.[6] The chloroform extracts were evaporated to dryness, wet oxidised with nitric and perchloric acids, and lead

was determined in the residues after dissolution in water by the dithizone procedure. Determinations of lead in reagents alone were carried out, and additions of lead in the range 5 to 10 μg were made to several samples to permit the recovery to be determined.

In all these experiments recovery of lead was low and erratic. During the extractions, precipitates of sulphur appeared owing to decomposition of the diethyldithiocarbamate reagent in acidic solution, and repeated extractions of the sample solution did not increase the recovery of lead. A further investigation of these findings is reported under "Limitations to the Extraction of Lead with Diethylammonium Diethyldithiocarbamate" below.

EXTRACTION OF LEAD WITH DIBENZYLDITHIOCARBAMATE—

In view of the above results, the use of other di-substituted dithiocarbamic acids of greater stability in acidic solution was considered. One of these, dibenzyldithiocarbamic acid, which has previously been used for extracting copper[6,8] from molar acid solutions was prepared from *NN*-dibenzylamine and carbon disulphide in the form of a 1 per cent. chloroform solution. To eliminate possible segregation effects, samples of a nominally lead-free 25 per cent. nickel - 20 per cent. chromium steel that had been prepared from high-purity stock material by vacuum melting were obtained and used for further experimental work. A modified method was used for dissolving the sample. Samples (5 g) were taken and, after dissolution in dilute perchloric acid and oxidation with hydrogen peroxide, were made up to a volume of 50 ml. Aliquots (10 ml) were taken and after dilution were reduced with hydroxylammonium chloride solution. The final acid concentration was about 0·5 M. The use of perchloric acid and the lower acidity used reduced the likelihood of re-oxidation of iron^{II} during the extraction procedure. Several extractions with 1 per cent. dibenzyldithiocarbamate solution in chloroform were carried out on the reagents alone, on aliquots of the sample and on aliquots to which 2·6 μg of lead had been added. After extraction of lead, the chloroform extracts were evaporated to dryness and wet oxidised, and lead was determined by dithizone as previously. The results obtained are given in Table I.

TABLE I

RECOVERY OF ADDED LEAD FROM 25 PER CENT. NICKEL - 20 PER CENT. CHROMIUM STEEL SOLUTIONS

Solution	Lead added, μg	Lead found, μg	Mean found, μg	Recovered, μg
Reagents only	Nil	3·3, 2·7, 2·3, 2·6, 3·5, 3·5, 2·8, 2·9, 3·2, 3·1	3·0	—
Sample solution, 10 ml (≡ 1 g of sample) ..	Nil	2·1, 2·6, 2·7, 2·9, 2·9, 2·8, 3·3, 3·0, 3·3	2·9	—
Sample solution, 10 ml ..	2·6	5·3, 4·8, 6·0, 6·0, 5·3, 5·4, 5·5, 5·0, 6·0	5·5	2·6
Sample solution, 10 ml ..	5·3	7·7, 8·2, 8·5, 8·1	8·1	5·2
Sample solution, 10 ml ..	10·6	13·9, 14·0, 14·0, 13·6, 13·5, 12·8, 13·1, 14·0, 13·6	13·6	10·7

With a standard deviation of $\pm$0·4 μg of lead on both blank and sample tests, the method appeared to be suitable for determining lead down to the level of 3 p.p.m. in 25 per cent. nickel - 20 per cent. chromium alloy steels with an accuracy of $\pm$1 p.p.m. No interference was noted from the presence of up to 0·1 per cent. of copper, cobalt, molybdenum, titanium, vanadium, tungsten and up to 0·05 per cent. of tin. Bismuth, however, is extracted together with lead, and in its presence an amended dithizone technique must be adopted. Details are given under "Procedure," p. 280.

LIMITATIONS TO THE EXTRACTION OF LEAD WITH DIETHYLAMMONIUM DIETHYLDITHIOCARBAMATE—

After the development of the dibenzyldithiocarbamic acid technique for extracting lead, further work was carried out to investigate the low and erratic recoveries obtained when lead was extracted from reduced acidic solutions with diethylammonium diethyldithiocarbamate. To permit a direct comparison of reagent efficiencies to be obtained, experimental conditions adopted were as under "Extraction of Lead with Dibenzyldithiocarbamate" above, *i.e.*, extraction from a reduced 0·5 M perchloric acid solution, but with diethylammonium diethyldithiocarbamate[6] substituted for dibenzyldithiocarbamic acid. The recovery of 10·6 μg

of lead was determined in the presence of the reagents alone and in the presence of 10 ml of lead-free sample aliquots (≡1g of 25 per cent. nickel - 20 per cent. chromium sample). Corrected for the appropriate blank values, results obtained were as follows—

Reagents alone *plus* 10·6 μg of lead	10·4, 10·6 and 10·7 μg of lead recovered
Lead-free aliquot of sample, 10 ml, *plus* 10·6 μg of lead	6·6, 9·7, 10·4, 7·1 and 11·6 μg of lead recovered

Although good recoveries of lead were obtained in the presence of the reagents alone, results were again erratic in the presence of the sample aliquot. An examination of the residues from the extraction of lead after wet oxidation of organic matter showed the presence of considerable amounts of nickel. Approximately 0·04 to 0·06 g of nickel were found to be co-extracted with lead under the experimental conditions adopted. The higher nickel concentrations that correspond to almost complete consumption of the reagent by nickel coincided with the lower recoveries of lead. The irregular interference from co-extracted nickel appears to eliminate diethylammonium diethyldithiocarbamate as a reagent for the preliminary separation of lead in the analysis of stainless and heat-resisting steels of high nickel content.

Method

Reagents—

All reagents should be of analytical grade. De-mineralised water should be used for the preparation of solutions and throughout the procedure.

De-mineralised water—Resistivity greater than 3×10^6 ohms per cm.

Perchloric acid, 72 per cent. w/w.

Hydroxylammonium chloride solution, 20 per cent. w/v, aqueous.

Hydrogen peroxide, 30 per cent. w/v.

Nitric acid, sp.gr. 1·42.

Dibenzyldithiocarbamate solution, 1 per cent. w/v in chloroform—Dissolve 4·2 ml of *NN*-dibenzylamine in 25 ml of chloroform. Transfer the solution to an amber-glass bottle. Add, with swirling, 0·6 ml of carbon disulphide dissolved in 25 ml of chloroform. Set the bottle aside overnight. This stock solution is stable for about a week. Just before use dilute 10 ml of stock solution to 100 ml with chloroform.

Ammonia solution, 50 per cent. v/v—Dilute 50 ml of ammonia solution, sp.gr. 0·88, to 100 ml with de-mineralised water.

Potassium cyanide solution, 5 per cent. w/v, aqueous.

Ammonium citrate solution—Dissolve 25 g of citric acid in 50 ml of water, add a few drops of thymol blue indicator and then ammonia solution, sp.gr. 0·88, to a final pH of 9·6 (yellow-blue). Finally dilute the solution to 150 ml with water.

Dithizone solution, 0·0008 per cent. w/v, in carbon tetrachloride—Transfer 0·010 g of dithizone to a 100-ml calibrated flask. Make up to the mark with carbon tetrachloride and dissolve the dithizone by shaking the flask in the cold. This solution is stable for 3 to 4 days. Just before use dilute 20 ml of this stock dithizone solution to 250 ml with carbon tetrachloride.

Phthalate buffer solution, pH 3·4—Dissolve 4·0 g of potassium hydrogen phthalate in 200 ml of water, and adjust the pH to 3·4 with diluted (1 + 9) hydrochloric acid.

Procedure—

All apparatus used should be soaked overnight in diluted (1 + 1) nitric acid and rinsed with water before use.

Weigh 5·000 g of sample millings into a 250-ml squat beaker, add 22 ml of perchloric acid and 20 ml of water. Warm the beaker on a hot plate until the sample has dissolved. Cool the solution and add dropwise, with swirling, 5 ml of hydrogen peroxide. Simmer the solution for 15 minutes. Cool it, and transfer quantitatively to a 50-ml calibrated flask. Make up to the mark with water and mix thoroughly. Transfer a 10-ml aliquot of sample solution by pipette into a 100-ml squat beaker, add 30 ml of water and then 10 ml of hydroxylammonium chloride solution. Warm the solution on a hot plate until evolution of gas occurs and simmer gently for 5 minutes to complete reduction of iron. Cool the solution rapidly in running water and transfer to a 100-ml separating funnel. Rinse the beaker twice with 2 to 3 ml of water. Add 10 ml of the dibenzyldithiocarbamate solution in chloroform to the sample solution in the extraction funnel and shake the funnel for 1 minute. Run the

lower organic layer into the original 100-ml beaker and repeat the extraction with a further 10 ml of reagent solution. Combine the organic extracts and evaporate them slowly to dryness on a steam-bath. Cover the beaker and add 5 ml of nitric acid, sp.gr. 1·42, to the residue and simmer gently until nitrous fumes are removed. Add 3 ml of perchloric acid and evaporate slowly to fumes until the vigorous oxidation reaction commences. When the reaction has subsided, draw back the cover glass and fume off residual perchloric acid to a final volume of about 0·5 ml. Cool the residue, add 7·0 ml of water and boil the mixture for 2 to 3 minutes to dissolve the residue. Cool and transfer the solution to a 100-ml separating funnel. Rinse the beaker twice with 2 to 3 ml of water. Add 2 ml of the hydroxylammonium chloride solution and then 5 ml of ammonium citrate solution, swirling while adding the reagents. Add a few drops of thymol blue indicator and adjust the pH to 9·6 (yellow-blue) with 50 per cent. ammonia solution. Add 3 ml of ammonia solution in excess, swirl and add 5 ml of potassium cyanide solution. Add 25 ml of the dithizone solution in carbon tetrachloride and shake the funnel for 2 minutes to extract lead. Filter the lower organic layer through a Whatman No. 541 filter-paper into a 4-cm Spekker cell and determine the optical density of the extract on a Spekker by using an Ilford spectrum green filter No. 604. Use a similar 4-cm cell containing carbon tetrachloride as a reference solution. Correct the optical density obtained for a reagent blank solution carried throughout the entire procedure. Determine the lead content of the sample aliquot by reference to a standard calibration curve prepared by carrying aliquots of a standard lead solution containing 2·0, 4·0, 6·0, 10 and 15 μg of lead through the dithizone extraction procedure.

PROCEDURE IN THE PRESENCE OF BISMUTH—

Interference from bismuth may be eliminated by using the procedure given below.[9] Transfer the dithizone extract containing lead and bismuth to a 100-ml separating funnel and add 25 ml of phthalate buffer solution. Shake the funnel to extract lead into the aqueous phase. Run off the lower organic layer and discard it. Repeat the extraction of the aqueous layer with 5 ml of the dithizone solution in carbon tetrachloride. Run off the lower organic layer and discard it. Add a few drops of thymol blue indicator and add 50 per cent. ammonia solution to a pH of 9·6 (yellow-blue). Add 3 ml of ammonia solution in excess and then 5 ml of the potassium cyanide solution. Extract lead by adding 25 ml of the dithizone solution in carbon tetrachloride and shaking for 2 minutes. Run the lower organic layer through a Whatman No. 541 filter-paper into a 4-cm Spekker cell, and determine the optical density of the extract as described previously. Correct for a blank solution carried through the procedure. Good separations and recoveries of 5·3 μg of lead in the presence of 10 μg of bismuth were obtained by this procedure (recovery = 6·6 and 6·4 μg of lead).

RESULTS

Owing to the lack of suitable standard alloy steels, the only possible direct comparison of results by this method and by others previously used is on synthetic solutions.

TABLE II

DETERMINATION OF LEAD IN 20 PER CENT. NICKEL - 25 PER CENT. CHROMIUM STEEL (M236)

Method	Lead, p.p.m.	
	Sample	Blank solution
Carrier sulphide separation	11,11	21,* 12†
Iron extraction, chromium volatilisation procedure ..	4, 8	21,‡ 21‡
Dibenzyldithiocarbamate extraction	10, 11, 12	3*

* AnalaR reagents.
† "Low-in-lead" reagents.
‡ Micro-analytical reagents.

Determinations were, however, carried out on British Chemical Standard 273 and British Chemical Standard 275 mild steel, residual standards containing $0{\cdot}003_0$ per cent. of lead (uncertificated) and $0{\cdot}005_0$ per cent. of lead (certificated), respectively. Determinations were carried out on individual sample weights of from 0·3 to 0·5 g. The volume of solvent perchloric acid used was adjusted to give a final acid concentration of 0·5 M after reduction and dilution.

Values found on replicate determinations are given below—

Sample	Recovered, per cent. of lead
B.C.S. 273	0·0037, 0·0037, 0·0037, 0·0036
B.C.S. 275	0·0059, 0·0058, 0·0059

Determinations were also carried out on a 20 per cent. nickel - 25 per cent. chromium steel (M236) by different methods. The results obtained are given in Table II.

Conclusion

The use of dibenzyldithiocarbamate permits lead to be rapidly separated from major elements present in 25 per cent. nickel - 20 per cent. chromium alloy steels before its subsequent determination with dithizone. Low blank values associated with its use permit concentrations of down to 3 p.p.m. of lead to be determined with an accuracy of ± 1 p.p.m. A considerable gain on time and sensitivity is obtained compared with methods involving sulphide separations or selective removal of interfering elements.

The work described above has been carried out as part of the General Research Programme of the National Physical Laboratory, and this paper is published by permission of the Director of the Laboratory.

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The Determination of Caesium-137 in Herbage and Soil

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A method is described for determining caesium-137 in samples of herbage and soil. The sample, with added caesium carrier, is treated either by wet ashing with nitric and perchloric acids (herbage) or by fusion with alkali (soil). The resulting solution is acidified and passed through a column containing a mixture of ammonium dodecamolybdophosphate and asbestos. Caesium is retained on the column, together with some potassium, which is separated by selective elution. Finally, the ammonium dodecamolybdophosphate is dissolved and the caesium precipitated as the chloroplatinate, which is mounted and its β-radiation counted.

The potential hazard of strontium-90 has been recognised for over 20 years, and many laboratories throughout the world are engaged in determining this element in rain-water, foodstuffs and soil. Among the long-lived fission products, caesium-137 is second only to strontium-90 in importance, as it also readily enters food chains and accumulates in the human body.

The disposal of radioactive wastes from establishments of the United Kingdom Atomic Energy Authority is carried out in accordance with authorisations agreed with the Ministry of Agriculture, Fisheries and Food and the Ministry of Housing and Local Government. These authorising Ministries normally require that a programme of environmental monitoring be carried out in the district surrounding each establishment from which there are discharges of gaseous and particulate radioactive wastes into the atmosphere. The purpose of these monitoring programmes is to ensure that people living in the surrounding area are not exposed to either radiation or radioactive materials at levels higher than those considered acceptable by competent authorities. The monitoring programme of the Atomic Energy Research Establishment specifies that samples of milk, herbage and root mat (arbitrarily defined as the top $1\frac{1}{2}$ inches of soil cores) shall be analysed for both strontium-90 and caesium-137. Although satisfactory procedures for determining strontium-90 in such materials have been established for some time, methods for determining caesium-137 have received comparatively little attention. Its measurement in samples of milk is most conveniently accomplished by γ-ray scintillation spectrometry, although radiochemical methods have been proposed.[1] The cow secretes only a few γ-ray emitting fission products in milk, and as most of these are short-lived, it is comparatively easy to make accurate determinations of caesium-137 in such samples. Herbage and soil, however, are normally contaminated with many medium- and long-lived fission products, in addition to natural γ-ray emitters, such as members of the uranium and thorium series, beryllium-7 and potassium-40, so that accurate determinations of caesium-137 from the complex γ-ray spectra cannot easily be achieved.

Attempts were made to determine the caesium-137 in root mat with a method similar to that described by Löw and Edvarson,[2] in which a normalised γ-ray spectrum of underlying soil ($1\frac{1}{2}$ to 6 inches in depth) is subtracted from that of the corresponding sample of root mat. If the caesium-137 is all contained in the root-mat horizon, then its photopeak is revealed in the difference spectrum, and its activity may be calculated, after suitable calibration, from either the height or area of this peak. Studies by Mercer and Ellis[3] of the downward movement of caesium-137 in soil have shown that in 1963 there was considerable penetration of caesium-137 to depths greater than 2 inches, and in such circumstances this technique cannot be used.

Radiochemical methods for determining caesium-137 in herbage and soil were therefore developed, and are described in this paper. They are both based on the same principle, in which the sample, with added caesium carrier, is brought into solution and, after acidification, passed through a column containing ammonium dodecamolybdophosphate mixed with an equal weight of asbestos to give adequate porosity.[4] Smit, Robb and Jacobs[5] have shown that, under these conditions, the only cations that exchange with ammonium dodecamolybdophosphate are those that form insoluble molybdophosphates (*i.e.*, potassium, rubidium, caesium, silver, mercury[I] and thallium[I]). The most strongly retained of these cations is

caesium, and its affinity is such that it is quantitatively retained, even in the presence of a large excess of potassium ions. Thus, in one step, the bulk of the inactive and contaminating radioactive material is effectively separated from the caesium. The method developed can be conveniently considered in four stages—

(*a*) Initial treatment of the sample to obtain the caesium-137 in solution and in equilibrium with added carrier.

(*b*) The dissolved sample is passed through a column containing ammonium dodecamolybdophosphate on which all the caesium and some of the potassium is retained.

(*c*) Selective elution of the potassium, leaving the caesium on the column.

(*d*) Recovery of caesium from the ammonium dodecamolybdophosphate, and its isolation in a form suitable for β-radiation counting.

Experimental

Initial treatment of samples—

Herbage—Three methods for extracting caesium-137 from samples of dried herbage were investigated. These included (*a*) complete dissolution by wet ashing with nitric and perchloric acids, (*b*) leaching with 3 M nitric acid and (*c*) dry ashing of the sample and subsequent extraction of the ash with hydrofluoric and perchloric acids. Several samples of herbage were analysed by each of these methods, and the highest and most consistent recoveries of caesium-137 were obtained with the wet-ashing treatment.

Soil—Earlier work in this laboratory showed that caesium-137 cannot be completely extracted from samples of soil by treating them with acids. Schulz, Overstreet and Barshad[6] have suggested that carrier-free caesium may be fixed in soils by precipitating the element on the surfaces of micaceous minerals. In the course of this precipitation, the existing crystal lattice is altered or extended slightly, so that the caesium is incorporated in a crystal structure. Under these conditions, the only way of ensuring that all the caesium-137 is in a soluble form and in equilibrium with the added carrier, is to subject the soil to fusion with alkali so that the mineral structure is destroyed. The fusion procedure adopted is similar to that described by Bryant, Morgan and Spicer[7] for extracting strontium-90 from samples of soil.

In some initial experiments, 20 mg of caesium carrier and a known amount of caesium-137 were added to a sample of soil, which was then dried at 110° C. The dry material was added in small portions to molten sodium hydroxide in a nickel crucible, and it was evident that some of the sample was lost from the crucible during the vigorous initial reaction. On leaching the melt, it was found that about 15 per cent. of the added caesium-137 had been lost during the fusion process. A more satisfactory procedure involved ashing of the sample and added caesium carrier at 400° C until the organic matter was destroyed. A low ashing-temperature was used, as it has been shown[8] that loss of caesium-137 occurs when samples are ashed at temperatures exceeding 450° C. The resulting ash is mixed with sodium hydroxide pellets and the mixture heated slowly over a Meker burner until a homogeneous melt is obtained. Under these conditions, only 5 per cent. of the caesium is lost during the fusion. After being cooled, the melt is leached with hot water and the insoluble material removed by centrifugation. The residue may be retained for determining strontium-90 if required. The supernatant liquid is acidified, and the precipitated silica removed by filtration. The filtrate is then passed through a column containing ammonium dodecamolybdophosphate on which the caesium is retained.

Preparation of ammonium dodecamolybdophosphate columns—

The ammonium dodecamolybdophosphate used in all these experiments was prepared by the method of Smit, Jacobs and Robb,[9] which gives a uniform crystalline product, individual crystals having a diameter of about 10 μ. Samples of commercially available ammonium dodecamolybdophosphate were found to consist of smaller crystals (2 to 5 μ) that were not so satisfactory for this application. Columns are prepared by mixing equal weights of ammonium dodecamolybdophosphate and asbestos, making the mixture into a slurry with 0·1 M ammonium nitrate and placing the slurry in glass tubes fitted with sintered-glass discs of porosity 1. Experiments with a solution containing caesium-137 and 20 mg of caesium carrier showed that a flow-rate of 1 ml per minute per sq. cm can be used without loss of caesium from the column.

SELECTIVE ELUTION OF POTASSIUM—

The amount of soil that can be analysed conveniently is limited by the fusion step to 20 g. In 1963, levels of caesium-137 in samples of local surface soil (0 to 1½ inches in depth) averaged about 1 pC per g dry weight. Under these conditions, it is necessary to use low-level β-radiation counting techniques to achieve adequate sensitivity. As shown in Table I, both potassium and rubidium contain natural β-ray emitting nuclides, so it is essential that adequate decontamination from these alkali metals is achieved. The separation of caesium from potassium is achieved by selective elution of the latter from the ammonium dodecamolybdophosphate column. The amount of rubidium in samples of herbage will be too small to contribute to the β-radiation count from the caesium-137, but an additional purification stage is introduced in the analysis of soil, as the amount of rubidium-87 in such samples could conceivably contribute to the β-ray activity of the separated caesium.

TABLE I

NATURALLY OCCURRING RADIONUCLIDES OF POTASSIUM AND RUBIDIUM

Element	Natural radionuclide	Radiation and energy	Half-life, years
Potassium	^{40}K	β-rays, 1·33 MeV γ-rays, 1·46 MeV	$1·39 \times 10^{9}$
Rubidium	^{87}Rb	β-rays, 0·27 MeV	$4·3 \times 10^{10}$

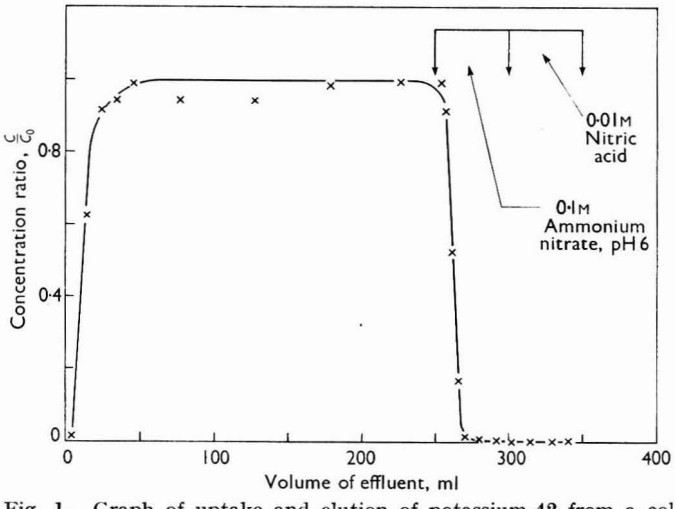

Fig. 1. Graph of uptake and elution of potassium-42 from a column of ammonium-12 molybdophosphate

To study the elution of potassium from ammonium dodecamolybdophosphate - asbestos columns, experiments were carried out with pile-produced potassium-42, which is a convenient radioactive tracer for potassium. A solution was prepared that contained about 1·3 g of potassium in 250 ml of dilute nitric acid. After 20 mg of caesium carrier and potassium-42 tracer had been added, the solution was passed through an ammonium dodecamolybdophosphate - asbestos column. Successive fractions of the effluent were collected and the potassium-42 concentration measured by means of γ-ray scintillation spectrometry. The ratio of the concentration in the effluent, C, to that in the original solution, C_0, for the various fractions, is shown in Fig. 1. This shows that the column rapidly becomes saturated with potassium, most of which is not retained. Washing of the column with 50 ml of 0·1 M ammonium nitrate effectively removes the remaining potassium from the column. A final wash with 0·01 M nitric acid is used to remove the excess of ammonium ions from the column before ammonium dodecamolybdophosphate is dissolved. Molar ammonium nitrate will remove rubidium as well as potassium from the column, but the concentration was restricted to 0·1 M in this procedure, since incomplete removal of ammonium ions could result in the co-precipitation of ammonium chloroplatinate with the caesium.

RECOVERY OF CAESIUM—

Smit[10] showed that caesium can be eluted from ammonium dodecamolybdophosphate columns with saturated ammonium nitrate solution, but that large volumes are required to effect complete removal. A more satisfactory procedure involves dissolving the ammonium dodecamolybdophosphate in sodium hydroxide solution and filtering off the asbestos. The filtrate is boiled to remove ammonia, and, after the pH has been adjusted to a value of 6, caesium chloroplatinate may be precipitated directly by the addition of chloroplatinic acid solution.

In a series of experiments, 1-g samples of ammonium dodecamolybdophosphate were dissolved in sodium hydroxide solution. After 20 mg of caesium carrier and a known amount of caesium-137 had been added, the solutions were boiled and adjusted to pH 6 with acetic acid. The solutions were cooled in ice, and caesium chloroplatinate was precipitated by adding 1 ml of 10 per cent. chloroplatinic acid solution. After 15 minutes, the precipitates were collected on weighed Whatman No. 42 filter-papers, washed with ethanol, allowed to equilibrate with the atmosphere, weighed and their β-radiation counted. The recoveries by the gravimetric and radiometric methods are compared in Table II and are seen to be in good agreement. Increasing the time of cooling beyond 15 minutes did not result in an appreciable increase in recovery.

TABLE II

COMPARISON OF RECOVERIES OF CAESIUM BY GRAVIMETRIC AND RADIOMETRIC METHODS

	Recovery, per cent., by—	
Sample No.	gravimetric method (as chloroplatinate)	radiometric method (as caesium-137)
1	91·6	91·9
2	92·2	91·5
3	83·7	85·2
4	95·7	93·4
5	94·0	93·4
6	94·7	93·2
Mean and standard deviation	92·0 $\pm$ 3·9	91·4 $\pm$ 2·9

RADIOMETRIC METHODS

Although this method for isolation proved to be satisfactory for recovering caesium from samples of herbage, a different procedure was used for soils to ensure complete separation from both inactive and radioactive contaminants. In this, the ammonium dodecamolybdophosphate is dissolved as before and the caesium co-precipitated, first as the cobaltinitrite and then as the bismuth iodide complex. The latter has been shown by Hara[11] to be highly specific for caesium and to give good decontamination from both potassium and rubidium. Finally, this complex is decomposed, and the caesium precipitated as the chloroplatinate for β-radiation counting. Recoveries of about 70 per cent. are obtained in the analysis of herbage and 60 per cent. in the analysis of soils.

METHOD

REAGENTS—

Caesium carrier solution, 10 mg of caesium per ml—Dissolve in water an accurately weighed amount of high-purity caesium chloride that has been dried for 30 minutes at 110° C.

Asbestos—For Gooch crucibles.

Sodium cobaltinitrite solution, 20 per cent. w/v—This solution should be freshly prepared before use.

Bismuth tri-iodide solution—Dissolve 20 g of bismuth tri-iodide and 20 g of sodium iodide in 50 ml of water and 2 ml of glacial acetic acid. Filter the solution if necessary and store it in a refrigerator.

Chloroplatinic acid solution, 10 per cent. w/v, aqueous.

Ammonium dodecamolybdophosphate—Dissolve 81 g of ammonium nitrate, 81 g of citric acid monohydrate and 102 g of ammonium paramolybdate in 2140 ml of water, without heating the solution. Pour this solution slowly with stirring into 850 ml of 7 M nitric acid in a 4-litre beaker to give a clear solution. Add 10 ml of a 5 per cent. solution of diammonium hydrogen orthophosphate with stirring, and then heat the solution to boiling. Continue stirring while boiling the solution for 2 minutes. Cool the solution for at least 30 minutes, and collect the ammonium dodecamolybdophosphate on a Buchner funnel. Return the filtrate to the original beaker, and wash the precipitate with M ammonium nitrate. To the filtrate add 50 ml of a 16 per cent. solution of ammonium paramolybdate, 5 ml of 7 M nitric acid and 10 ml of diammonium hydrogen phosphate solution. Heat the solution to boiling and filter it as before. The cycle may be repeated several times. Make all the ammonium dodecamolybdophosphate obtained into a slurry with M ammonium nitrate, collect it on a Buchner funnel and wash it repeatedly with portions of the same solution, until the pH of the washings is above 3. Finally, wash the precipitate with 0·1 M ammonium nitrate, suck it well dry and expose it to the air for several days until a fine, dry yellow powder is obtained. Mix the powder well and store it in a dark place.

PROCEDURE—

Preparation of dodecamolybdophosphate columns—Mix equal weights of ammonium dodecamolybdophosphate and asbestos in a beaker, and make the mixture into a slurry with 0·1 M ammonium nitrate. Pour the slurry into a glass tube fitted with a sintered-glass disc of porosity 1. Allow the suspension to settle under gravity. Tubes of 2-cm diameter are used for samples of herbage and tubes of 3-cm diameter for samples of soil.

Analysis of herbage—Add 2 ml of caesium carrier solution to 50 g of oven-dried herbage in a 1-litre conical flask. Moisten the sample to prevent ignition and add 16 M nitric acid in small amounts, with swirling, until the initial vigorous reaction has subsided. Heat the solution to boiling and add small amounts of fuming nitric acid until no more brown fumes are evolved. Cool the solution and add a mixture of 50 ml of 16 M nitric acid and 50 ml of 60 per cent. perchloric acid. (Care should be taken that all the herbage is oxidised before the nitric acid - perchloric acid mixture is added.) Continue heating the solution until the fumes of perchloric acid appear. Cool the solution, add 10 ml of 11 M hydrochloric acid and heat it almost to dryness. Cool the solution, dilute it to 200 ml and add 5 M sodium hydroxide until the solution is alkaline. Spin the suspension in a centrifuge, and wash the residue by making it into a slurry with 50 ml of water. Spin the slurry in a centrifuge, and combine the supernatant liquid with that obtained from the previous centrifugation. Adjust the pH of the solution to about 1 with 16 M nitric acid, and pass the solution, at a flow-rate not exceeding 2·5 ml per minute, through a column containing 1 g of each of ammonium dodecamolybdophosphate and asbestos. Wash the column with 50 ml of 0·1 M ammonium nitrate and then 50 ml of 0·01 M nitric acid, and discard the washings. Transfer the ammonium dodecamolybdophosphate and asbestos to a beaker and dissolve the ammonium dodecamolybdophosphate by adding sufficient 5 M sodium hydroxide. Filter off the asbestos, and boil the filtrate for 30 minutes to remove the final traces of ammonia. Adjust the volume to 50 ml, cool the solution in ice and adjust the pH to a value of 6 with glacial acetic acid. Add 1 ml of chloroplatinic acid solution and allow the solution to stand for 15 minutes, with occasional stirring. Transfer the contents of the beaker to a centrifuge tube and spin off the precipitate. Discard the supernatant liquid, make the precipitate into a slurry with water and filter the slurry on a weighed Whatman No. 42 filter-paper in a filter-stick. Wash the precipitate with ethanol and allow it to come to equilibrium with the atmosphere for at least 2 hours before weighing it to determine the caesium recovery. Mount the precipitate and filter-paper on an aluminium tray, and count the β-radiation in a counter previously calibrated with sources of various weights and known activities.

Analysis of soil—Add 2 ml of caesium carrier solution to 20 g of soil in a nickel crucible. Dry the mixture at 110° C in an oven and then ash it at 400° C in a muffle furnace. Add 60 g of sodium hydroxide pellets to the crucible and mix them thoroughly with the ash. Heat the crucible over a Meker burner, raising the temperature gradually so that none of the sample is lost by frothing. When the initial reaction has subsided, add 4 g of anhydrous sodium carbonate, and continue heating the mixture until a homogeneous melt is obtained. Cool the melt, and extract it with 500 ml of water. When the dissolution of the melt is complete, spin the solution in a centrifuge, and wash the residue twice with 50 ml of water.

Combine the supernantant liquids and acidify the mixture with 16 M nitric acid to a pH of about 1. Filter the gelatinous precipitate under vacuum with a filter-aid such as kieselguhr, if necessary. Wash the precipitate and combine the filtrates. Pass the solution, at a flow-rate not exceeding 4 ml per minute, through a column containing 2 g each of ammonium dodecamolybdophosphate and asbestos. Wash the column with 100 ml of 0·1 M ammonium nitrate and then 50 ml of 0·01 M nitric acid, and discard the washings. Wash the contents of the column into a beaker, and dissolve the ammonium dodecamolybdophosphate by adding 5 M sodium hydroxide. Filter off the asbestos, and boil the filtrate for 30 minutes. Cool the solution in ice, adjust the pH to about 6 with acetic acid, and precipitate the caesium by adding 2 g of sodium nitrite and an excess of sodium cobaltinitrite solution. Allow the

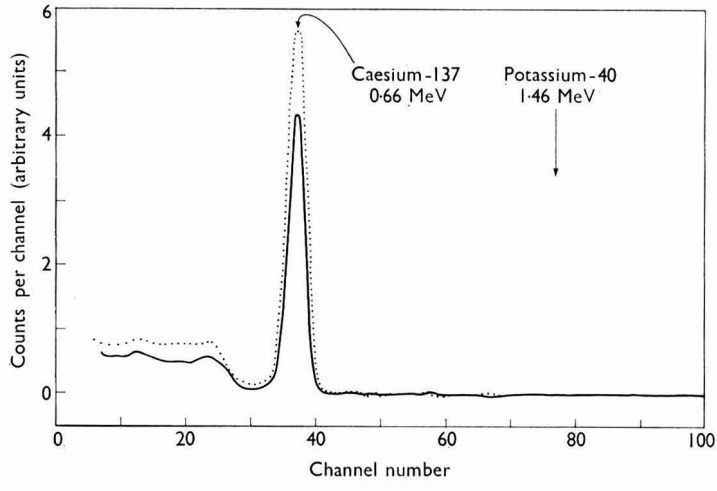

Fig. 2. γ-Ray spectrum of caesium chloroplatinate containing caesium-137 from herbage samples. Dotted line, caesium-137 from herbage samples; continuous line, caesium-137 from standard

solution to stand for 15 minutes with occasional stirring, and then spin it in a centrifuge. Discard the supernatant liquid, wash the precipitate by making it into a slurry with 10 per cent. acetic acid and spinning it in a centrifuge. Dissolve the precipitate by warming it with the minimum required volume of 4 M nitric acid. Dilute the solution to 10 ml and filter off any insoluble material. Neutralise the filtrate with 5 M sodium hydroxide and separate the cobalt precipitate by spinning the solution in a centrifuge. Wash the precipitate with 5 ml of water, spin it in a centrifuge and combine the supernatant liquids in a 20-ml beaker. Acidify the solution with glacial acetic acid and evaporate it to about 5 ml under an infrared lamp. Transfer the contents of the beaker to a centrifuge tube (the combined solution and washings should not exceed 8 ml in volume) and add 0·5 ml of glacial acetic acid. Cool the tube in ice and add 2 ml of bismuth tri-iodide solution. Continue cooling the tube for 5 minutes, with occasional stirring of the contents, and separate the caesium precipitate by spinning the tube and contents in a centrifuge. Discard the supernatant liquid and wash the precipitate with 10 ml of ice-cold wash solution, prepared by diluting 0·5 ml of bismuth tri-iodide solution to 10 ml with 10 per cent. acetic acid. Finally wash the precipitate with 10 ml of ice-cold ethanol. Dissolve the precipitate by boiling it with 4 ml of 4 M nitric acid until all the iodine is evolved. Dilute the solution to 20 ml with water and cool it in ice. Precipitate the caesium by adding 1 ml of chloroplatinic acid solution. Allow the suspension to stand for 15 minutes, with occasional stirring, and then spin it in a centrifuge. Make the precipitate into a slurry with water and filter the slurry through a weighed Whatman No. 42 filter-paper in a filter-stick. The remainder of the procedure is exactly as described for the analysis of herbage.

Discussion

In addition to caesium-137, it has been shown by Palmer and Perkins[12] that fallout from the testing of nuclear weapons contains caesium-134. This is a β-ray emitter with a

half-life of 2·2 years. Its activity in 1963 was only about 1 per cent. of that of the longer-lived caesium-137 in various samples, and its distribution appears to be world-wide. Morgan, Rundo, Vandervell and Emeleus[13] have also detected caesium-136, another radionuclide of caesium in samples of both rain-water and milk. The half-life of this radionuclide is only 13 days, however, and it will only be found during and shortly after a series of nuclear-weapon tests.

Samples of herbage may contain a whole range of fission-product and natural radionuclides. To show that these were all effectively separated from caesium on the ammonium dodecamolybdophosphate column and in the subsequent precipitation, several sources of caesium chloroplatinate, obtained from samples of herbage collected in 1963 and analysed by the method described above, were combined and their γ-ray scintillation spectrum measured. In Fig. 2, this is compared with that of a standard caesium-137 source, and it is clear that there is no significant contaminating γ-activity. Similarly, sources of caesium chloroplatinate isolated from samples of soil showed no significant γ-activity that could not be attributed to caesium-134 and caesium-137.

Measurements of caesium-137 in samples of herbage and soil collected in the vicinity of the Atomic Energy Research Establishment, Harwell, showed that the levels were no higher than would be expected from world-wide fallout deposition. The results of these determinations and of those of caesium-137 in milk have been reported by Vandervell, Mitchell and Morgan.[14]

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The Determination of Higher Alcohols in Potable Spirits: Comparison of Colorimetric and Gas-chromatographic Methods

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Gas chromatography of brandies and whiskies shows that n-propanol, isobutanol, 2-methylbutan-1-ol and 3-methylbutan-1-ol comprise the major proportion of the higher alcohols. The furfural method for determining higher alcohols described in the Report of the Royal Commission on Whisky and Other Potable Spirits, 1909, gives results in excess of the sum of these alcohols determined by gas chromatography, but the method of the Association of Official Agricultural Chemists, which involves the use of *p*-dimethylaminobenzaldehyde, gives results that agree well with those obtained by gas chromatography.

In his evidence to the Royal Commission on Whisky and Other Potable Spirits 1908–1909, Dr. T. E. Thorpe, then Government Chemist, described a method for determining higher alcohols in potable spirits based on the colour formed by the action of furfural and sulphuric acid. The method had been developed under Dr. Bell, the previous Government Chemist, to meet the need for a rapid method suitable for examining samples submitted by H.M. Customs & Excise. Since that time, the method has been further described by Simmonds[1] and Nicholls,[2] and has gained a semi-official status in this country. Consistent results are not easily obtained without long practice, and discrepancies between results obtained in different laboratories prompted an investigation by Osborn and Mott,[3] who recommended several changes, the most important being the use of heat for developing the colour. When applied to samples of commercial spirits, this modification, however, was found by this Laboratory to lead to apparently excessively high results (A. J. Blake in a private communication). Recently it has been remarked that the Royal Commission method gives results that are high compared with those given by other methods,[4] and it is evident that a means of obtaining a more accurate indication of the actual higher-alcohol content is required. Many methods have been described and are in use in different laboratories, but until the development of gas chromatography it has been impossible to assess the accuracy of these methods without long and tedious investigation.

The present work demonstrates that the method described by Boruff,[5] and now the official method of the Association of Official and Agricultural Chemists,[6] provides results in substantial agreement with those obtained from gas-chromatographic determinations carried out in this Laboratory.

Experimental

Reagents—

p-*Dimethylaminobenzaldehyde*—AnalaR grade.

Isopentanol, purified for milk testing—The alcohol was washed with 2 per cent. sulphuric acid, 2 per cent. aqueous sodium hydroxide and water in turn, dried over anhydrous sodium sulphate and redistilled. The middle third of the distillate was used, and gas chromatography with 10 per cent. of diethyl tartrate on a 100 to 120 mesh Celite column showed it to contain approximately 75 per cent. of 3-methylbutan-1-ol and 25 per cent. of 2-methylbutan-1-ol. Other alcohols were present to the extent of less than 3 per cent.

n-Butanol, s-butanol, isobutanol and n-propanol—These alcohols were general-purpose reagent grade and were treated similarly to the isopentanol, and contained less than 3 per cent. of other alcohols as demonstrated by gas chromatography.

Materials for gas chromatography—

Celite—Batches of Celite, nominally 100 to 200 mesh, were set aside in concentrated hydrochloric acid for at least 24 hours, and then washed with water until free from acid. After wet sieving to 120 mesh, the material was dried and set aside in 2 per cent. methanolic

sodium hydroxide for 24 hours. For polyester or ester columns, the Celite was washed free from alkali with methanol, but for stationary phases unlikely to be affected by alkali, the Celite was washed twice by decantation so as to leave a trace of alkali behind. Final drying was carried out in a vacuum oven.

STATIONARY PHASES—

Polyethylene glycol 400.
Dinonyl phthalate.
Squalane.
Diethyl tartrate—General-purpose reagent grade material was redistilled *in vacuo.*

PREPARATION OF COLUMNS FOR GAS CHROMATOGRAPHY—

The stationary phase was deposited on the Celite in the usual manner by evaporation from a suitable organic solvent. An infrared lamp was found to be a convenient source of heat for removing the solvent, and resulted in much less spitting than either a hot plate or water-bath. Final traces of solvent were removed in a vacuum oven. Columns were made from straight lengths of $\frac{1}{4}$-inch o.d. (0·2-inch i.d.) or $\frac{1}{8}$-inch o.d. (0·1-inch i.d.) soft-drawn copper tubing, and bent after packing. The columns were filled by alternately tapping and vibrating.

GAS CHROMATOGRAPHS—

A Perkin Elmer Model 451, with flame ionisation detector and a Perkin Model 800 dual-column programmed-temperature gas chromatograph were used.

COLORIMETRIC PROCEDURE—

A 100-ml portion of the sample measured at 60° F was transferred to a 400-ml flat-bottomed flask with the minimum of water (not more than 5 ml) and the flask fitted with an anti-splash still head and a revenue-type condenser. Distillation was carried out until about 5 ml remained undistilled, the flask that was used to measure out the sample also being used for collecting the distillate. The distillate was made up to 100 ml at 60° F with water, and the specific gravity of the resultant spirit determined at 60° F. The ethanol content of the original spirit was then found by reference to the appropriate tables.

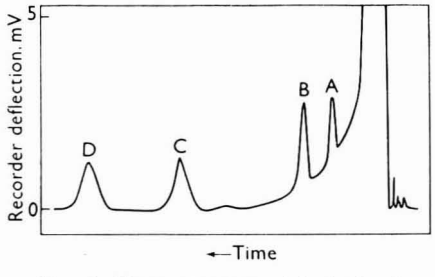


Fig. 1. Chromatogram of 5 μl of a brandy obtained with a 6-foot × $\frac{1}{8}$-inch i.d. column of 80 per cent. of Celite and 20 per cent. of polyethylene glycol 400 at 100° C. Carrier gas, nitrogen at a flow-rate of 15 ml per minute. Peak A, n-propanol; peak B, isobutanol; peak C, isopentanol; peak D, n-pentanol (internal standard)

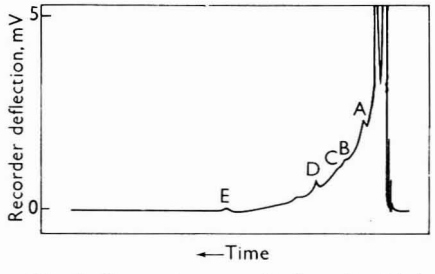


Fig. 2. Chromatogram of a brandy obtained with a 3-foot × $\frac{1}{4}$-inch i.d. column of 99 per cent. of glass beads and 1 per cent. of polyethylene glycol 400 at 150° C. Carrier gas, nitrogen at 45 ml per minute. Peak A, n-hexanol; peaks B and C, unknowns; peak D, furfural *plus* unknown; peak E, ethyl n-decanoate

The higher alcohols in a portion of the distillate were determined by the method described by Boruff[5] (the A.O.A.C. method). The samples examined contained about 40 per cent. by volume of ethanol, and colorimetric determination of the higher alcohols involved dilution of 5 ml of the distillate to 100 ml. The standards were accordingly made up in 2 per cent. v/v ethanol. Optical densities were measured at 530 mμ. This is the wavelength at which similar concentrations of isopentanol and isobutanol give rise to the same optical density on the instrument used.

A further portion of the distillate was examined by the original Royal Commission method. To an appropriate volume of sample distillate (or standard) in a 75-ml flask were added 0·5 ml of a 1·0 per cent. furfural solution and 10 ml of concentrated sulphuric acid so as to form a bottom layer. The contents of the flask were then mixed by gently rotating the flask first one way and then the other in an ice-bath for 30 seconds. After the mixture had been set aside for 1 hour, the colours formed were compared visually with a series of standards made up in 50 per cent. ethanol from an n-propanol - isobutanol - isopentanol - octanol (1+2+3+1) mixture.

Examination of potable spirits

By gas chromatography—

Fouassin[7] has examined quantitatively, by gas chromatography, various spiritous liquors. The sensitivity of the thermal detector used was such that larger volumes of sample than were desirable had to be injected on the columns, and also the response of this detector to water necessitated pre-treatment of the sample with a dehydrating agent.

Mecke and de Vries[8] used continuous extraction of the sample with a 1 + 2 mixture of n-pentane and diethyl ether to concentrate the sample and remove water, a technique that has also been used by Baraud,[9] and Sihto[10]; Dinsmore and Webb[11] concentrated wines by distillation. Pre-treatment of this kind is undesirable, and is unnecessary if the more sensitive flame ionisation detector is used.[12] Such a detector was used in this Laboratory and direct injection of the untreated sample on to the column was therefore possible. In spite of the non-volatile matter present, it has been found that over a period of 2 years the injection block has required cleaning only once.

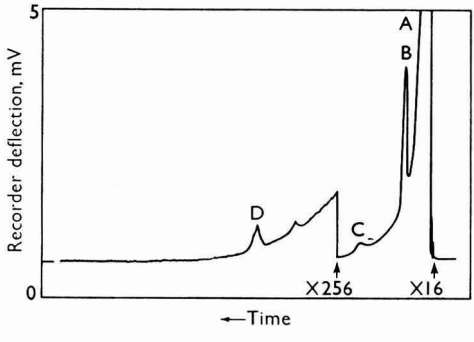


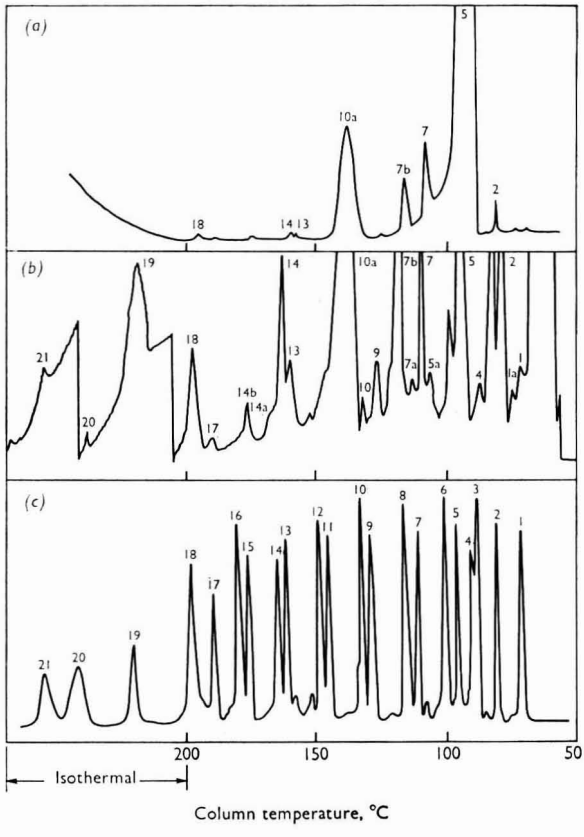
Fig. 3. Chromatogram of a brandy obtained with a 3-foot × $\frac{1}{8}$-inch i.d. column of 90 per cent. of Celite and 10 per cent. of squalane at 75° C. Carrier gas, nitrogen at a flow-rate of 15 ml per minute. Peak A, ethanol; peak B, isopentanol; peak C, ethyl n-hexanoate *plus* unknown; peak D, ethyl n-decanoate

The preliminary investigations were carried out with a 20 per cent. polyethylene glycol 400 column at 100° C. The major higher-alcohol peaks due to n-propanol, isobutanol and isopentanol were observed (see Fig. 1), together with occasional traces of n-butanol and, in marc brandies, appreciable amounts of s-butanol. On a diethyl tartrate column the isopentanol was resolved into two peaks corresponding to 2-methylbutan-1-ol and 3-methylbutan-1-ol. For the remainder of this paper, the isopentanol is treated as a single compound, because the two alcohols concerned are for practical purposes alike in their behaviour in the colorimetric processes. Further examination on dinonyl phthalate, diethylhexyl sebacate and glycerol columns served to demonstrate that the higher-alcohol peaks from the polyethylene glycol column could be attributed solely to the appropriate alcohols and were not contributed to by substantial amounts of other compounds. There was no evidence of important proportions of isopropanol. Alcohols having a longer retention time than the pentanols were not easily detected under the conditions used because of the reduction in peak height with increasing

retention volume. These compounds in potable spirits may be made to give significant peaks by using—

(*i*) high column temperatures,
(*ii*) a lower proportion of stationary phase to column support,
(*iii*) a less polar stationary phase,
(*iv*) temperature-programmed gas chromatography.

Fig. 2 is a chromatogram of a brandy obtained with a column of 1 per cent. of polyethylene glycol on glass beads at 150° C; Fig. 3 is a chromatogram of a brandy obtained with a non-polar column, 10 per cent. of squalane on silanised Celite; Figs. 4 (*a*), (*b*) and (*c*) were obtained under temperature-programmed conditions, and show, respectively, chromatograms of a brandy, of an ether - pentane extract of the same brandy and of a mixture of aliphatic alcohols and esters for comparison. The conclusion drawn from the above and many similar chromatograms is that for most purposes the total higher-alcohol content may be taken as the sum of the C_3 to C_5 alcohols, the alcohols above C_5 being present in amounts too small to be significant for the purposes of routine anslysis.



Key to Peaks

1	ethyl formate
1a	acetone
2	ethyl acetate
3	ethyl formate
4	methanol
5	ethanol
5a	s-butanol
6	ethyl butyrate
7	n-propanol
7a	isopentyl acetate
7b	isobutanol
8	ethyl valerate
9	n-butanol
10	ethyl n-hexanoate
10a	isopentanol
11	n-pentanol
12	ethyl n-heptanoate
13	n-hexanol
14	ethyl n-octanoate
14a	s-octanol
14b	furfural
15	n-heptanol
16	ethyl nonanoate
17	n-octanol
18	ethyl n-decanoate
19	ethyl undecanoate
20	n-decanol
21	ethyl laurate

These peak assignations are tentative

Fig. 4. Chromatograms of (*a*) a brandy, direct injection, (*b*) an ether - pentane extract of the same brandy and (*c*) a mixture of alcohols and esters. The chromatograms were obtained on a Perkin-Elmer Chromatograph with a 6-foot × $\frac{1}{8}$-inch i.d. column of 90 per cent. of Celite and 10 per cent. of polyethylene glycol 400 programmed for column temperatures of 50° C increasing at 6·25° C per minute, up to 200° C

The first quantitative determinations were accordingly carried out on polyethylene glycol 400 columns and relied on constant delivery from Hamilton syringes to permit direct comparison to be made with standard mixtures, the syringes being checked from time to time by weighing an expressed volume of liquid. Over a long period it was found that changes in retention volumes due to ageing of the column and to the impossibility of maintaining

precisely constant operating conditions, necessitated careful re-standardisation. An internal standard, pure n-pentanol, was therefore introduced into the samples as a solution in 40 per cent. v/v ethanol containing 500 mg of n-pentanol per 100 ml. One millilitre of this solution was mixed with 10 ml of sample. In spite of minor variations in column conditions it was found that consistently good results were obtained when 5-μl samples were used for injection. A typical calibration graph is shown in Fig. 5. The large excess of ethanol and water in the

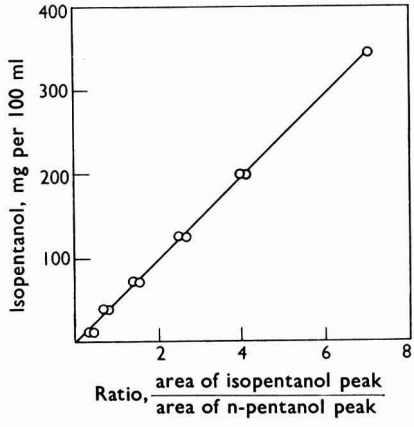


Fig. 5. Graph of relation between the proportion of isopentanol and the ratio of the peak height of isopentanol to that of the internal standard, n-pentanol

samples causes the retention times of the other compounds present to be different from those obtained when pure materials are injected. It was therefore essential to make up the standards in 40 per cent. v/v ethanol to simulate the spirit strength of the samples (brandy, whisky and rum), which in this country are almost invariably 70° proof.

TABLE I

HIGHER-ALCOHOL CONTENT OF A WHISKY

Higher-alcohol content as determined by successive injections, mg per 100 ml of ethanol in sample			
n-Propanol	Isobutanol	Isopentanol	Total
50·2	98·3	76·9	225
50·2	98·3	80·8	229
54·2	102·7	80·8	238
50·0	96·8	80·0	227
48·1	96·7	75·7	221
50·1	98·3	77·0	225
48·2	96·8	77·0	222
		Mean ..	*229*

The consistency of the results obtained is shown in Table I, which gives the variation in response to consecutive injections of the same sample. The main results are considered later.

COLORIMETRIC DETERMINATION—

When the Royal Commission method was used, comparison with standards was made visually because, in our opinion, this method is not suited to spectrophotometry. Results are expressed to the nearest 25 parts by weight per 10^5 parts by volume of ethanol in the sample, *i.e.*, mg per 100 ml.

Results from the A.O.A.C. (Boruff[5]) method are expressed to the nearest 10 parts per 10^5.

At least two determinations by each of these methods were made on each sample and the results are given in Table II.

Discussion

The shortcoming of all colorimetric methods for determining higher alcohols in potable spirits lies in the impossibility of reproducing the composition of the sample in the standard. Errors may be introduced because the different alcohols present give rise to different colours and because of side reactions between the reagent and non-alcoholic components. These errors are particularly noticeable with the Royal Commission method, with which the colours formed vary from reds through purples to blues, and with which for instance gins, which contain only small amounts of higher alcohols, give rise to fairly intense colours. In the A.O.A.C. method, colours are compared spectrophotometrically at the wavelength at which the optical densities due to equal concentrations of isobutanol and isopentanol are identical, and therefore the proportion of these alcohols one to another in the sample, or for that matter

Table II

Comparison of the higher-alcohol content of spirits as determined by three methods

	Higher alcohols, mg per 100 ml of ethanol in sample, found by—		
	Royal Commission method	A.O.A.C.	Gas-chromatographic method
Whisky—			
	400	200	200
	425	220	210
	575	280	250
Rum—			
	75	20	20
	75	5	5
Brandy—			
	400	260	230
	800	370	350
	700	360	380
	1000	390	400
	700	430	490
	850	320	360
	925	370	390
	925	370	350
	300	220	240
	650	290	300
	950	330	350
	1600	500	470
	1200	470	510
	1500	330	370
	850	430	430

in the standard, is irrelevant. Table III gives the optical density due to various alcohols relative to the standard when put through the A.O.A.C. colorimetric procedure. The contribution of n-propanol to the optical density at 530 mμ is about one-fifth of that of the standard, and the total higher alcohols are therefore, theoretically, underestimated by about four fifths of the n-propanol present. In practice, although the A.O.A.C. figure were generally lower than the gas-chromatographic figures, the error was not serious, because in the samples examined the propanol did not account for more than 20 per cent. of the total higher alcohols. (Detailed results of the gas-chromatographic investigation will be published elsewhere.) The other higher alcohols are present in extremely small proportions and do not contribute significantly to the optical density, and it is also evident that side reactions do not take place to any great extent. For the Royal Commission method, however, we have reason to believe that side reactions do take place, *e.g.*, removal of aldehydes from the spirits by preliminary heating under reflux with *m*-phenylenediamine can considerably reduce the colour intensity given by the samples. Similar treatment has only a small effect on the colours produced by the A.O.A.C. method.

The results obtained by using the A.O.A.C. method and gas-chromatographic methods are therefore in substantial agreement, although the figures obtained by the Royal Commission method are always considerably higher. In extenuation of the Royal Commission method, however, it must be pointed out that in the course of his evidence, Dr. Thorpe acknowledged that the figures obtained thereby did not always agree with those obtained by other means,

and that the main reasons for its use were rapidity and the facility it afforded for comparison with the very large amount of data that had been compiled in the Government Laboratory over many years. In this latter respect, where such data is available, its use remains justified,

TABLE III

COMPARISON OF OPTICAL DENSITY OF EQUAL CONCENTRATIONS OF VARIOUS ALCOHOLS AT 530 mμ

Alcohol	Optical density	Alcoho	Optical density
n-Propanol	0·2	Isopentanol	1·0
Isopropanol	0·2	n-Hexanol	0·8
n-Butanol	0·2	n-Octanol	0·8
Isobutanol	1·0	s-Octanol	0·7
s-Butanol	0·3	n-Decanol	0·3
n-Pentanol	0·8	2-Phenylethanol ..	0·1

but in other circumstances, and especially where comparison between analyses in different laboratories is to be made, the A.O.A.C. method is preferable.

We thank Mr. H. Baxter for carrying out some of the experimental work in connection with this investigation and the Government Chemist and the Department of Scientific and Industrial Research for permission to publish this paper.

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SHORT PAPERS

The Ultrapurification of Hydrofluoric Acid

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From recent papers,[1,2,3,4] we noticed that it is usual to prepare pure hydrofluoric acid by distilling the analytical-reagent grade material. Stills made of platinum, polyethylene or polypropylene are used, as these materials are resistant to boiling hydrofluoric acid. The advantage of the method described by Coppola and Hughes[3] is that temperature of distillation is 70° to 85° C, and so boiling and entrainment of fine droplets by the vapour do not occur.

We found that the method of isothermal distillation, described for hydrochloric acid and ammonium hydroxide by Irving and Cox,[5] was extremely useful for preparing ultra pure hydrofluoric acid. The advantages of this method are—

(*i*) It is simple.
(*ii*) It can be carried out at room temperature.
(*iii*) There is little risk of contamination.

Method

Place in a polyethylene washing-bowl two 250-ml polyethylene beakers. Put in one beaker about 150 ml of concentrated technical-grade hydrofluoric acid (35 M, 75 per cent. v/v). Put in the second beaker about 150 ml of de-mineralised water.

Place a similar washing-bowl upside down on top of the first one, to make a close fit. The de-mineralised water will absorb hydrofluoric acid vapour, so that after a while, pure hydrofluoric acid is formed.

After 2 days, the pure acid is 12 M. By replenishing the impure acid, the pure acid can be concentrated to 25 M after another 2 days.

The efficiency of the method is demonstrated by the results given in Table I. The second and fifth columns give analyses of the technical-grade hydrofluoric acid (75 per cent. v/v). In the third and sixth columns, the analyses of the ultra pure hydrofluoric acid (50 per cent. v/v) are shown. These results were obtained from spectrochemical analysis[3,6] of the residue obtained after

Table I

Efficiency of ultrapurification method

Elements	Concentration, μg per ml, in residue of— 5 ml of technical-grade hydrofluoric acid	500 ml of purified hydrofluoric acid	Elements	Concentration, μg per ml, in residue of— 5 ml of technical-grade hydrofluoric acid	500 ml of purified hydrofluoric acid
Al	0·7	8×10^{-3}	Ga	<0·02*	$0{\cdot}1 \times 10^{-3}$
Ca	12	2×10^{-3}	In	<0·2*	$0{\cdot}1 \times 10^{-3}$
Mg	1	1×10^{-3}	Cd	<0·4*	$0{\cdot}1 \times 10^{-3}$
Fe	240	1×10^{-3}	Mn	0·4	$0{\cdot}08 \times 10^{-3}$
Pt	8	$0{\cdot}8 \times 10^{-3}$	B	0·06	$0{\cdot}06 \times 10^{-3}$
Cr	<0·2*	$0{\cdot}6 \times 10^{-3}$	Sn	0·12	$0{\cdot}04 \times 10^{-3}$
Ti	<0·06*	$0{\cdot}6 \times 10^{-3}$	Ge	<0·02*	$0{\cdot}04 \times 10^{-3}$
Zn	<0·6*	$0{\cdot}6 \times 10^{-3}$	Ag	0·18	$0{\cdot}004 \times 10^{-3}$
Pb	0·14	$0{\cdot}2 \times 10^{-3}$	Na	0·6	$<1 \times 10^{-3}$
Cu	0·18	$0{\cdot}1 \times 10^{-3}$	P	1·2	$<1 \times 10^{-3}$
Ni	0·12	$0{\cdot}1 \times 10^{-3}$	Au	1·2	$<0{\cdot}02 \times 10^{-3}$
			Si	0·2	$<0{\cdot}01 \times 10^{-3}$

* Limits of detection in 5-ml sample.

evaporation of 5 ml of technical-grade hydrofluoric acid or 500 ml of purified hydrofluoric acid in a platinum dish, till about 1 ml was left. This 1 ml was placed in a small platinum vessel, some drops of very pure nitric acid were added and the solution was evaporated almost to dryness. After addition of some drops of pure nitric acid, the concentrate was transferred to a wax-treated

graphite electrode and evaporated to dryness at about 50° C. The results obtained were corrected for the blank value.

Since the minute amounts of metallic impurities found in the distilled acid can hardly have been conveyed in the vapour, it is reasonable to assume that they are due to contamination from vessels or the atmosphere. The aluminium content is probably due to the use of polythene material.[4]

We thank Dr. N. W. H. Addink and Mr. A. W. Witmer for carrying out the spectrochemical analyses.

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The Colorimetric Determination of Isoniazid in the Presence of Sodium Aminosalicylate

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IN the report of the British Pharmaceutical Codex Revision Committee,[1] it was noted that an acceptable method for assaying sodium aminosalicylate and isoniazid cachets had not yet been established.

Up to the present we have found the method of Mitchell, Haugas and McRoe[2] to be the most useful, but even when every attempt has been made to reproduce the original conditions exactly, the importance of which has been emphasised by Kum-Tatt and Yan-Hon,[3] we have never been able to obtain as consistent recoveries as the originators. For these reasons, Akatsuka's report[4] of a new colour reaction for hydrazine derivatives with 2,3-dichloro-1,4-naphthaquinone, which was not subject to interference from aminosalicylates, was of particular interest. We have examined this reaction and we can now report that with certain precautions it can be applied to the rapid and accurate determinaton of isoniazid in mixtures or tablets containing isoniazid and sodium aminosalicylate.

EXPERIMENTAL

The method involves the reaction of isoniazid with 2,3-dichloro-1,4-naphthaquinone in the presence of potassium carbonate to form a blue colour, which was found, by plotting optical density against wavelength, to be due to a broad absorption band that had a diffuse peak at 605 mμ. This wavelength was chosen for all subsequent measurements.

When identical amounts of isoniazid were caused to react (*a*) in the presence of water alone and (*b*) in the presence of a solution of sodium aminosalicylate, the resulting optical densities at 605 mμ were identical. When the reaction was carried out on sodium aminosalicylate alone, the resulting colour was identical to the colour of the reagent blank solution, and the optical density of the solution was zero when measured against the reagent blank solution. These observations confirm that sodium aminosalicylate does not interfere in the reaction. We have found that calibration curves prepared on different occasions are linear up to a concentration of 20 μg of isoniazid per ml in the solution taken for measurement, but that the slope varies considerably. We take this to indicate that, although under given conditions, Beer's law is obeyed, the sensitivity of the reaction is highly susceptible to changes in conditions. We have found that order of addition of reagents, temperature of reaction and time of reaction are among the factors that may lead to variations in optical density.

ORDER OF ADDITION OF REAGENTS—

Akatsuka recommended the additions of potassium carbonate to a mixture of isoniazid solution with ethanolic reagent solution. We have observed that a reaction takes place in the absence of alkali which, if allowed to proceed for sufficiently long, or if accelerated by warming, leads to

the production of an orange compound that is not converted to the blue compound on the additions of alkali. Even if the additions of alkali are delayed for as little as 10 minutes, the blue colour is reduced by about 14 per cent. In the recommended procedure we have therefore stipulated that the reagent should be added to a solution that has already been made alkaline, so that the desired colour-forming reaction begins immediately, and the side reaction is prevented or greatly reduced.

TEMPERATURE OF REACTION—

Solutions were prepared for colorimetric measurement with a standard isoniazid solution, to give a concentration in the final mixture of 10 μg per ml, by using the recommended procedure, except that the temperatures were adjusted to known values before mixing, and the mixtures were maintained at the same temperature. After being set aside for 20 minutes, the solutions were rapidly warmed to room temperature, and their optical densities were measured at 605 mμ. The greater sensitivity of the colour produced at the low temperatures could be clearly seen, and there was no apparent change in intensity when the solutions were brought to room temperature. The results, which demonstrate clearly that the final optical density is affected by the temperatures at which the colour-forming reaction takes place, are given below—

Temperature of reaction, °C	0	6	10·5	17	20
Optical density measured in 1-cm cells	0·730	0·730	0·710	0·615	0·630

TIME OF REACTION—

It was established that with the reaction taking place at room temperature the colour intensity rises to a maximum value after about 17 minutes and stays constant for a further 10 minutes, after which time it begins to fade slowly. The colour of the blank solution formed in the absence of isoniazid rises to a maximum after 17 minutes and stays constant for at least a further 50 minutes.

METHOD

REAGENTS—

2,3-*Dichloro*-1,4-*naphthaquinone solution*—Prepare a 0·03 per cent. w/v solution in absolute ethanol.

Potassium carbonate solution—Prepare a 0·1 per cent. aqueous solution from anhydrous analytical-reagent grade material.

PROCEDURE—

Take a weight of sample expected to contain 50 mg of isoniazid. For "Cachets of Sodium Aminosalicylate and Isoniazid B.P.C.," the appropriate weight is 2·3 to 2·4 g. Dissolve the sample in 1 litre of water. If the solution is not clear, owing to the presence of tablet excipients, allow the solution to settle, and filter it, collecting about 10 ml of filtrate.

Simultaneously prepare a solution containing 50 mg of isoniazid per litre as a standard. Ensure that the standard and sample solutions are at the same temperature, within the range 20° to 25° C.

Transfer with a pipette 4 ml of each solution and 4 ml of water to act as a reagent blank into 20-ml calibrated flasks. Add to each, at 5-minute intervals, starting with the blank solution, 5 ml of potassium carbonate solution followed immediately by 5 ml of dichloronaphthaquinone solution. When any effervescence has subsided, dilute each to the mark. Measure the optical densities of the sample and standard solutions in 1-cm cells against the blank at 605 mμ at exactly the same time (which must be between 20 and 25 minutes) after the addition of the reagents.

CALCULATION—

The percentage of isoniazid in the sample is given by—

$$\frac{A}{B} \times \frac{50}{\text{Weight, in grams, of the original sample taken}}$$

where A is the optical density of sample solution and
B is the optical density of standard solution.

RESULTS

To evaluate the method, a blend of sodium aminosalicylate with 2·438 per cent. of isoniazid, *i.e.*, in the ratio 40 to 1, was prepared in the laboratory. This, in our experience, is the ratio in which the mixture of these two drugs is most commonly prescribed, as, for example, in cachets each containing 2 g of sodium aminosalicylate with 50 mg of isoniazid.

Three analysts each carried out four determinations by Mitchell, Haugas and McRoe's method and by the modified Akatusa method as described above. The results are shown in Table I.

TABLE I

DETERMINATION OF ISONIAZID IN ADMIXTURE WITH SODIUM AMINOSALICYLATE: COMPARISON OF RESULTS BY TWO METHODS

	Proposed method			Mitchell, Haugas and McRoe's method		
Analyst	Isoniazid, per cent.	Mean	Standard deviation	Isoniazid, per cent.	Mean	Standard deviation
A	2·39 2·40 2·39 2·48	2·41	0·043	2·54 2·50 2·59 2·58	2·55	0·036
B	2·42 2·50 2·44 2·39	2·44	0·047	2·55 2·49 2·49 2·43	2·49	0·049
C	2·44 2·43 2·47 2·45	2·45	0·010	2·45 2·46 2·44 2·44	2·45	0·012
Combined results		*2·43* (*99·8 per cent. recovery*)	*0·034*		*2·50* (*102·3 per cent. recovery*)	*0·032*

The recovery value given by the proposed method is much closer to the theoretical value. The difference between the overall means is highly significant (Student's $t = 4{\cdot}77$) indicating a genuine improvement in accuracy. There appears to be virtually no difference in precision. The method is both rapid and convenient, and is now in routine use in this laboratory.

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Spectrophotometric Determination of Beryllium with Beryllon III

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A RECENT review on the analytical chemistry of beryllium[1] has shown that the two most important reagents for the routine spectrophotometric determination of beryllium are Chrome azurol S (C.I. Mordant Blue 29) and Beryllon II.[2] Fast sulphon black F (C.I. No. 26990) has since been proposed as a selective chromogenic reagent for beryllium,[3] but has several serious disadvantages, including long colour-development time and a narrow analytical range. In addition, since the reagent blank solution has a higher optical density than the beryllium complex, measurements must be made with the beryllium sample solution in the reference cell. Kuznetsov, Bol'shakova and Fang[4] investigated several hydroxyazo compounds as chromogenic reagents for beryllium and concluded that Beryllon III, 5-(4-diethylamino-2-hydroxyphenylazo)-4-hydroxynaphthalene-2,7-disulphonic acid, was one of the most suitable. We have made a detailed study of Beryllon III for the determination of beryllium, and, in the presence of triethanolamine and EDTA as masking agents, found it to be superior to Beryllon II and Chrome azurol S.

Method

Apparatus—

A Hilger Uvispek spectrophotometer was used for all optical-density measurements.

Reagents—

Beryllon III—Synthesise Beryllon III from H-acid (4-amino-5-hydroxynaphthalene-2,7-disulphonic acid) and *m*-diethylaminophenol as described previously.[4] Prepare a 0·020 per cent. solution by suspending 0·050 g of Beryllon III in 25 ml of water and 0·25 ml of 10 per cent. sodium hydroxide solution, stirring to dissolve, and diluting the solution to 250 ml.

Complexing solution—Dissolve 10 g of EDTA (disodium salt) in 80 ml of water, add 6 ml of triethanolamine, and dilute it to 100 ml.

Procedure—

Transfer by pipette a portion (5 ml or less) of the slightly acidic sample solution, containing less than 10 μg of beryllium, into a 50-ml calibrated flask. On a separate portion determine the amount of 10 per cent. sodium hydroxide solution required to neutralise the free acidity. Add 2·5 ml of complexing solution, 2·0 ml of 10 per cent. sodium hydroxide *plus* the pre-determined amount of sodium hydroxide, and set the solution aside for 5 minutes. Dilute the solution to about 35 ml, and set it aside for a further 5 minutes. Add 10·00 ml of 0·020 per cent. Beryllon III solution, and dilute the solution to the mark. Measure the optical density of the solution in a 1-cm cell at 526 mμ against a reagent blank solution. In the presence of iron^{III}, manganese, chromium^{III}, thorium or zirconium, readings should be made within 10 minutes.

Results

The beryllium - Beryllon III complex exhibits a broad absorption peak with a maximum at 526 mμ, when measured against a reagent blank solution. Beer's law is obeyed from 0 to 0·18 μg of beryllium per ml and the complex has a molecular extinction coefficient of 19,200 at

Table I

Interference with beryllon III

Beryllium taken, 5 μg

Foreign ion	Amount taken, mg	Beryllium found, μg	Relative error, per cent.	Foreign ion	Amount taken, mg	Beryllium found μg	Relative error, per cent.
Al	2	5·0	0	Sn^{4+}	2	5·0	0
	5	5·1	+2	Th	0·5	5·0	0
	10	5·2	+4		1	4·7	−6
Ba	2	5·0	0		2	4·5	−10
Ca	2	5·0	0	Ti	0·5	5·3	+6
Cd	2	5·0	0	U^{6+}	2	5·3	+6
Co	2	5·0	0		5	5·5	+10
Cr^{3+}	2	4·8	−4	V^{5+}	2	5·1	+2
Cu	2	5·2	+4	W^{6+}	2	4·9	−2
	5	5·4	+8	Zn	2	5·0	0
	10	5·7	+14	Zr	2	4·3	−14
Fe^{3+}	2	5·0	0	F^-	20	5·0	0
	5	4·9	−2	PO_4^{3-} ..	2	5·0	0
Hg^{2+} ..	2	5·2	+4	NaCl ..	200	5·1	+2
Mg	2	5·0	0	$NaClO_4$ ..	200	5·0	0
Mn	2	4·7	−6	$NaNO_3$ ..	200	5·0	0
	5	4·2	−16	Na_2SO_4 ..	200	5·0	0
Mo^{6+} ..	2	4·9	−2	NH_4Cl ..	200	5·1	+2
Ni	2	5·0	0				
Pb	2	5·0	0				

526 mμ, corresponding to 0·00047 μg of beryllium per sq. cm on the Sandell scale. The range over which Beer's law is obeyed can be extended by using a higher reagent concentration, but 0·004 per cent. Beryllon III solution was selected as a practical limit, since at this concentration the optical density of the blank solution *versus* water is already quite high (0·91). The colour is

stable for at least 48 hours, and has a temperature coefficient of −0·4 per cent. per °C in the range 15° to 35° C. Readings on a series of standards showed the relative standard deviation at the level of 0·10 μg of beryllium per ml to be ±0·4 per cent.

TABLE II

EFFECT OF TIME ON RECOVERY OF BERYLLIUM IN THE PRESENCE OF FOREIGN IONS

Beryllium taken, 5 μg

Foreign ion	Amount taken, mg	Beryllium found, μg, after— 10 minutes' standing	30 minutes' standing
Fe^{3+}	2	5·0	5·0
	5	4·9	4·8
Mn	2	4·7	4·5
	5	4·2	3·8
Cr^{3+}	2	4·8	5·2
Th	0·5	5·0	5·0
	1	4·7	4·8
	2	4·5	4·7
Zr	2	4·3	4·8

TABLE III

COMPARISON OF METHODS

Reagent	Molar extinction coefficient (wavelength in parenthese)	Range over which Beer's[6] law is obeyed, μg per ml
Beryllon III	19,200 (526 mμ)	0 to 0·18
Beryllon II	12,000 (630 mμ)	0·08 to 0·32*
Chrome azurol S	6,300 (569 mμ)	0 to 2·0

* Beer's law not strictly obeyed.

TABLE IV

COMPARISON OF INTERFERENCES

Foreign ion*	Relative error, per cent. Beryllon III (5 μg of beryllium per 50 ml)	Beryllon II (10 μg of beryllium per 50 ml)	Chrome azurol S (20 μg of beryllium 50 per ml)
Al	0	+6	+5
Ca	0	0	+2
Cr^{3+}	−2	>+100	>+100
Cu	+2	+9	+11
Fe^{3+}	0	+4	0
Mg	0	0	−2
Mn	−3	+5	+3
Mo^{6+}	−1	0	0
Ni	0	+4	+7
Th	−6	−33	+7
U^{6+}	+3	−2	+11
V^{5+}	+1	+4	+14
W^{6+}	−1	+4	0
Zn	0	0	0
Zr	−7	–	+7
PO_4^{3-}	0	–	−4
NaCl†	+2	−7	−3
$NaClO_4$† ..	0	−2	+2
$NaNO_3$† ..	0	−7	−3
Na_2SO_4†	0	−2	−14

* Weight ratio of foreign ion to beryllium = 200 to 1.
† Amount of foreign ion added = 200 mg.

A study of interferences is shown in Table I. Only titanium and large amounts of manganese and zirconium cause significant interference. A variation of ±0·4 ml of 10 per cent. sodium

hydroxide solution added in the recommended procedure produced no change in the optical-density readings. The formation of ferric and manganese hydroxides was prevented by using a small portion of sample and a high initial concentration of sodium hydroxide.[5] The optical density was decreased with time by iron^{III} and manganese, and increased with time by chromium^{III}, thorium and zirconium. There is no significant change in the optical-density readings within 10 minutes of mixing, and the changes that occur after 30 minutes are given in Table II.

COMPARISON WITH BERYLLON II AND CHROME AZUROL S—

The sensitivities and analytical range of the Beryllon III, Beryllon II and Chrome azurol S methods for the spectrophotometric determination of beryllium are compared in Table III, and the effect of some foreign ions is shown in Table IV. On the basis of sensitivities and freedom from interferences, particularly chromium, Beryllon III is clearly superior to the other two reagents, although sometimes the wider analytical range of Chrome azurol S may be advantageous.

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A Simplified Method for Determining Fibrous Residue in Wheat Meals and in Brown and Wholemeal Breads

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THE determination of crude fibre by the Weende method as proposed by Henneberg[1] a century ago has been the subject of much criticism and although many attempts have been made to replace it by other simpler methods, it is still the official method today.[2]

This official method is used extensively for policing provisions of Pure Food Acts, which lay down certain levels of crude fibre for brown and wholemeal breads.

Criticism of the official method is directed at the time required for carrying out the determinations and the many possible sources of error rather than at the empirical nature of the method.

A simpler and shorter method has now been developed that yields results identical with those obtained by the official method when applied to wheat meals and to brown and wholemeal breads.

The proposed method is based on the use of dimethylsulphoxide, which has been shown to dissolve starches and many proteins[3,4] and is now commercially available.

EXPERIMENTAL

It was found that mixtures of dimethylsulphoxide and formic acid dissolve crushed wheat almost entirely, leaving behind the husk. Samples of wheat meal were treated under reflux with dimethylsulphoxide and formic acid in varying proportions in an attempt to find a mixture that would give the same result as the official crude-fibre method. The hot digestion mixture was filtered through a sintered-glass filter crucible under suction.

METHOD

APPARATUS—

Sinter crucibles G2, approximately **35**-*ml capacity.*
Sinter glass plates, porosity G1.
Erlenmeyer flasks, **250**-*ml capacity.*
Air-condenser.

REAGENTS—

Dimethylsulphoxide.
Formic acid, **99** *per cent. w/w*—Analytical-reagent grade.
Formic acid solution, **30** *per cent. v/v, aqueous.*

PROCEDURE—

Air dry and crush the sample. Place a mixture of 150 ml of dimethylsulphoxide and 45 ml of 99 per cent. formic acid in a 250-ml Erlenmeyer flask. Weigh out 1 g of the sample and transfer it to the flask, so that the sample floats on the digestion mixture (see Note 1).

Attach the air-condenser and heat the mixture under reflux briskly for 45 minutes under a fume hood with gentle shaking during the first few minutes of boiling to break up any lumps of sample.

TABLE I

COMPARISON OF METHODS

Proposed method		Official (Weende) method
Number of determinations	Crude fibre, per cent. on dry basis, mean value	Crude fibre, per cent on dry basis, mean of duplicate determinations
Bread—		
3	1·41	1·38
5	1·86	1·78
3	1·64	1·56
3	1·81	1·85
2	1·46	1·45
2	0·44	0·45
Wheat meals—		
3	1·55	1·60
2	2·20	2·20
2	2·19	2·26
2	2·79	2·68

Remove the flame and after the boiling has subsided remove the air-condenser. Filter the liquid rapidly by suction through a conditioned and weighed crucible of a capacity of about 35 ml with a sinter-plate of porosity G2 and an additional sinter-plate of porosity G1 (see Notes 2 and 3). Transfer any particles left in the flask to the filter by washing the flask immediately with portions of boiling 30 per cent. aqueous formic acid, dislodging particles adhering to the walls of the flask with a rubber-tipped glass rod. Wash the fibre in the crucible with about 100 ml of boiling formic acid solution and then with 100 ml of boiling water. When the crucible is cool, rinse it with several portions of acetone.

Dry at 105° C for 3 hours, cool and weigh.

Experiments have shown that the amount of ash in the fibre isolated by this method is negligible and may be ignored. De-fatting of the sample before analysis is not necessary.

NOTES—

1. If the sample is put into the flask first, it will stick to the bottom on addition of the solvent mixture and will be difficult to dislodge. Particles adhering to the bottom of the flask will char during digestion, and the vigorous shaking necessary to dislodge the sample will leave particles adhering to the wall of the flask, away from the bulk of the digestion mixture.

2. It was observed that as the reaction mixture cooled, gel formation took place to such an extent that the filter was blocked. Rapid filtration through crucibles with G1 sinter-plates was unsatisfactory because sometimes losses of very finely divided fibre occurred. However, G2 sinter-plates proved to be too dense to permit rapid filtration as the fine fibre particles blocked the filter pores. This difficulty was overcome by placing a snugly fitting G1 sinter-plate on top of the G2 plate of the crucible. Sufficient fine fibre is caught on the G1 plate to prevent the G2 plate underneath from being blocked.

3. Prepare the sinter-crucible by trimming a sinter-plate of porosity G1 (sinter-plates of various porosities are commercially available) until it fits snugly on top of the sinter-plate of a G2 sinter-plate crucible. The G1 plate must lie flat on the G2 plate. The G2 crucible is conditioned and weighed with the G1 sinter-plate in place.

4. Dimethylsulphoxide may be recovered in good yield from the filtrate of the crude-fibre determination, obtained before the washing of the fibre with 30 per cent. aqueous formic acid. To the cold filtrate, add sufficient solid sodium carbonate to neutralise the formic acid, and filter the mixture. Vacuum-distil the filtrate and discard the first fractions. Pure dimethylsulphoxide distils over at about 81° C at the pressures obtained with the water-pump.

RESULTS

Some results obtained by the proposed method compared to results obtained by the official A.O.A.C. method are given in Table I.

Statistical analysis and conclusions

An analysis of variance, performed by the method of Yates,[6] showed that the difference between the two methods is within the limits for replicate determinations over the range of values in the present investigations, namely from 0·44 to 2·76 per cent.

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Quantitative Determination of Aflatoxin in Groundnut Products

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The examination of raw materials used in animal feeding stuffs for the presence of aflatoxin, a poison associated with some groundnut products, takes much time and effort. The pressing need has been for a method that would permit a determination of aflatoxin to be carried out in a simple and speedy manner. This has now been achieved. Briefly, it involves the extraction of the toxin from the ground meal by chloroform in the presence of water at laboratory temperatures. A determination can be carried out on a de-fatted meal in less than 1 hour. The assessment of the amount of toxin is made by using thin-layer chromatographic plates of Kieselgel G, as in the published literature.[1,2,3,4]

Previous methods for extracting the toxin from the meal involved prolonged boiling with organic solvents. The slowness of the extraction was thought to be because of protection of the toxin, perhaps by a protein complex or by the nature of the cell structure. It was thought necessary to change the structure in some way so as to permit the toxin to be available for solution, and it was found that the swelling that takes place when water is added to the meal causes sufficient disruption for rapid dissolution of the toxin in chloroform to occur.

It was found, when a toxic groundnut meal was tested for fibre by the method of the Fertiliser and Feeding Stuffs Act, that the acid filtrate contained most, if not all, of the aflatoxin, and that it was readily extracted from the acidic water by chloroform.

Starting with this fact, many extractions were carried out with hot and cold, faintly acidic and alkaline solutions, and water, in the presence of chloroform. Meals of varying toxicity, on which determinations by the conventional methanol-extraction techniques had been made, were used. It was found that water (distilled was used for the sake of consistency) proved to act in a manner similar to the acidic and alkaline solutions, and was subsequently used in further tests.

In the early experimental work most of the tests were carried out as described below—

A 10- or 20-g portion of the ground, de-fatted meal was put into a bottle of 200 to 250-ml-capacity to which was added cold water, equivalent to about ten times the weight of the meal. The mass was then shaken until it was completely wetted, after which it was shaken by repeatedly inverting the bottle for 30 minutes. Chloroform, 50 or 100 ml, was then added and the shaking repeated for a further 10 minutes. The chloroform was recovered either by centrifugation or by means of a separating funnel, after which the aflatoxin was determined directly in this solution by thin-layer chromatography as in the published literature.

It was found that the results obtained by the water - chloroform method were in agreement with those obtained when any of the lengthy methanol methods was used. Occasionally the former yielded slightly the higher results.

Some typical results are given below—

Aflatoxin by methanol method, p.p.m.	8	0·25	5 to 6	<0·04
Aflatoxin by water - chloroform method, p.p.m. ..	8	0·25	5 to 6	<0·05

It was therefore established that the water - chloroform technique was completely effective in extracting the toxin from de-fatted cakes and meals. Repeating the work on the same samples without first removing the oil yielded the same results, although one sample contained over 3 per cent. of oil.

All of the meals yielded virtually colourless chloroform extracts.

It was found occasionally that the chloroform settled to give a coarse emulsion, and it was it was necessary to spin the mass in a centrifuge for a short time in order to obtain a clear extract.

The work was continued to see whether, by altering the technique, the formation of emulsions and the need for centrifugation could be avoided. It was found that the ratio of water to meal used in the earlier work could be drastically decreased, and instead of ten parts of water to one part of meal, a one-to-two water - meal ratio was used in the manner described below.

A 10- to 20-g weighed amount of meal was well mixed with half its weight of water. This was usually done by stirring the mixture in a bottle. The water wetted the meal well and was absorbed to give a granular mass that was easy to handle. Chloroform, 50 or 100 ml, was added, and, after a moment or two of vigorous shaking, the mixture was further shaken or swirled for 30 minutes. The mass was then filtered, and an aliquot of the clear chloroform extract tested by thin-layer chromatography. It has been established that if the chloroform is added immediately after the meal is wetted with water, then the toxin is dissolved in a matter of minutes. About 50 per cent. of the chloroform used was recovered by simple filtration, and 70 to 75 per cent. when a Buchner funnel was used.

TABLE I

AMOUNT OF MATERIAL EXTRACTABLE BY DIFFERENT SOLVENTS AND EXTRACTION TECHNIQUES

Sample	Solvents	Method of extraction	Time of extraction	Soluble matter, per cent.	Aflatoxin, p.p.m.	Colour* of extract
Toxic meal	50 ml of $CHCl_3$	Cold shaking	30 minutes	1·25	0·2	A
Toxic meal	5 ml of H_2O + 50 ml of $CHCl_3$	Cold shaking	30 minutes	1·5	8	A
Imported meal	50 ml of $CHCl_3$	Cold shaking	30 minutes	3·4	0	A
Imported meal	5 ml of H_2O + 50 ml of $CHCl_3$	Cold shaking	30 minutes	3·8	0·25	A
Toxic meal, de-fatted	$CHCl_3$	Soxhlet	3 hours	1·1	8	A
Imported meal, de-fatted	$CHCl_3$	Soxhlet	3 hours	0·7	0·25	A
Toxic meal, de-fatted	MeOH	Soxhlet	3 hours	13·3	—	B
Imported meal, de-fatted	MeOH	Soxhlet	3 hours	15·9	—	B
Toxic meal, de-fatted	50 ml of $CHCl_3$	Cold shaking	30 minutes	0·5	—	A
Toxic meal, de-fatted	5 ml of H_2O + 50 ml of $CHCl_3$	Cold shaking	30 minutes	0·5	—	A
Imported meal, de-fatted	50 ml of $CHCl_3$	Cold shaking	30 minutes	1·25	—	A
Imported meal, de-fatted	5 ml of H_2O + 50 ml of $CHCl_3$	Cold shaking	30 minutes	1·25	—	A
Toxic meal	MeOH	Soxhlet	3 hours	14·4	8	B
Imported meal	MeOH	Soxhlet	3 hours	20	0·25	B
Toxic meal†	MeOH	Soxhlet	3 hours	16·4	—	B
Imported meal†	MeOH	Soxhlet	3 hours	21·8	—	B
Toxic meal	Light petroleum	Soxhlet	3 hours	1·1	0	A
Imported meal	Light petroleum	Soxhlet	3 hours	3·2	0	A

* A ≡ colourless to pale yellow; B ≡ brown.
† Preliminary treatment with 5 ml of water.

The above experimental work naturally led to the use of the same principle for preparing extracts for dosing ducklings. The amount of meal taken for extraction depends upon the style of dosing used. Generally, the extract from 80 g of meal is required for dosing one duckling; the method can be applied in three ways.

(*a*) Take 80 g of de-fatted meal and mix it well with 40 ml of water. Shake the mixture with 400 ml of chloroform. Filter the mixture through a Buchner funnel fitted with suitable paper, and wash the meal with several portions of chloroform. Combine the chloroform extracts and evaporate them to dryness, finishing with vacuum or under nitrogen. Disperse them in water to give a concentration suitable for dosing ducklings.

(*b*) Carry out the wetting described in method (*a*), then extract the meal in thimbles in a Soxhlet extraction apparatus for about 2 hours. Combine the chloroform extracts and continue as in (*a*).

(*c*) Where sufficient material is available, the amount of meal may be increased to, say, 120 g, and an aliquot of the filtered chloroform equal to 80 g of meal taken and evaporated. The rest may be used for testing, so that the exact concentration in the emulsion actually used for dosing will be known.

The work described above has been carried out with extracted meals and expelled cakes. The test worked equally well with groundnut kernels that had been de-fatted by the normal procedure, *i.e.*, with light petroleum or hexane.

It is advisable, however, to test the recovered oil by treating the light-petroleum extract for the recovery of any aflatoxin that might be present.

It is mentioned above that the chloroform extracts are invariably almost colourless, whereas the methanol extracts are usually quite dark. In addition to this difference, the amounts of matter extractable by the two solvents are widely different. This is shown in Table I.

I thank the Milling Group Administration, Unilever Limited, for permission to publish this paper.

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The Determination of Carbon and Hydrogen in Organic Compounds Containing Mercury

By T. F. HOLMES and A. LAUDER

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A literature survey has revealed that most methods reported for the determination of carbon and hydrogen in organic compounds containing mercury are based on slow combustion procedures. During the combustion, elemental mercury is retained temporarily by fillings of the Pregl universal type, but will in subsequent determinations pass on to the absorption train, resulting in high hydrogen values. This has been overcome by using gold wire in the beak end of the combustion tube.[1,2,3,4] Ingram[5] used a boat containing ceric oxide, litharge, silver dichromate, silver oxide and lead chromate placed immediately after the ceria - copper oxide - lead chromate combustion catalyst.[6] A rapid method based on the cobalto-cobaltic oxide method of Vičeřa[7,8] has been developed by Garwargious and Macdonald.[9] The exit tube and beak end are packed with tightly coiled gold wire to remove the mercury. It is necessary to regenerate the gold after 5 to 6 determinations.

The "rapid" empty-tube method[10] is used for all carbon and hydrogen determinations in this laboratory and it is for this reason that this method has been developed.

Initially, attempts were made to remove the mercury by packing the beak end of the combustion tube with gold foil. These failed, presumably owing to the short contact time. Correct carbon and hydrogen values were obtained when gold deposited on Gooch-crucible asbestos, and for convenience loosely packed into a Flaschentrager tube, was placed between the beak end of the main combustion tube and the water-absorption tube.

Method

Heat some Gooch-crucible asbestos in a crucible (800° to 1000° C) for several hours, then cool and soak it in a saturated ethereal solution of auric bromide. Pump off the ether and replace the asbestos in the crucible and heat it, gently at first and then more strongly, for 3 hours. The bromine is lost quite readily. Pack loosely a Flaschentrager tube with the gold-impregnated

asbestos, which is held in position with plugs of quartz-wool. Place the tube in the absorption train and flush it with oxygen. The tube is then ready for use. By using between 7- and 10-mg samples and an oxygen flow-rate of 150 ml per minute, the combustion is completed in about 5 minutes, and flushing of the apparatus takes 10 minutes. In all, a determination takes 30 minutes.

Discussion and results

Numerous determinations have been carried out without it being necessary to regenerate the gold-impregnated asbestos. Although it might be expected that there would be some loss of water in the tube of gold-impregnated asbestos, as this is not heated, in fact with prolonged flushing at the flow-rate specified such a discrepancy does not occur.

Some typical results are given in Table I.

Table I

Results of the determination of carbon and hydrogen in various compounds

Compound*	Carbon content, per cent.— calculated	Carbon content, per cent.— found	Hydrogen content, per cent.— calculated	Hydrogen content, per cent.— found
$[MeHgPMe_3]Cl$	14·5	14·7	3·70	3·73
$[MeHgPMe_2Ph]Cl$	27·8	27·5	3·60	3·66
$[MeHgPEt_3]Br$	20·3	20·5	4·35	4·50
$[MeHgPMe_2Ph]I$	22·5	22·5	2·94	2·92
$[EtHgPMe_3]Cl$	17·6	17·4	4·13	4·23
$[EtHgPEt_3]Br$	22·5	22·5	4·71	4·75
$[nPrHgPMe_3]Cl$	20·3	20·2	4·54	4·60
$[nPrHgPMe_2Ph]Cl$	31·7	31·5	4·35	4·30
$[nBuHgPMe_3]Cl$	22·8	22·7	4·91	4·81
$[nBuHgPMe_2Ph]Cl$	33·4	33·4	4·67	4·74
$[nBuHgPMe_3]I$	18·25	18·1	3·91	3·86
$[MeHgdipy]NO_3$	30·45	30·4	2·55	2·55
$[MeHgAsPh_3]ClO_4$	36·7	36·95	2·90	2·90
$[MeHgPPh_3][Cr(NH_3)_2(SCN)_4]$	34·8	34·9	3·05	3·15
$(PEt_3)_2HgBr_2$ (12 results)†	24·15	24·2 ± 0·1	5·07	5·13 ± 0·14

* The preparation of all the compounds listed has been described by Coates and Lauder[11].

† This compound has been used as a standard for the determination of carbon and hydrogen.

Conclusions

The proposed method gives satisfactory results that are within the accepted limits of accuracy. It permits the analysis of mercury compounds to be carried out relatively rapidly and removes the necessity of more than one combustion apparatus when the "rapid" empty-tube method is normally used for carbon and hydrogen analyses. When a mercury-containing compound is submitted for analysis, the tube of gold-impregnated asbestos is flushed with oxygen, placed in the absorption train and a mercury-containing standard analysed before the analysis of the unknown compound is attempted.

One of us (A.L.) thanks the Ethyl Corporation for a research studentship.

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Book Reviews

METHODES D'ANALYSE, CETEMA—1964. METHODES 101 À 150. COMMISSARIAT À L'ÉNERGIE ATOMIQUE. Pp. vi + 249. Paris: Presses Universitaires de France. 1964.

This is the second collection of methods published by CETEMA, the first hundred methods having been issued in 1962. The methods are those that have been found acceptable in the French "Commissariat à l'Energie Atomique; commission d'etablissement des methodes analytiques." Great care has been taken to draw up the methods in a uniform style, and each has been tested in two or more laboratories to make sure that the descriptions are adequate, clear and precise. Interfering elements are listed, and the estimated precision of each method is also stated. Each description is self-contained, there are few cross-references.

No discussions of underlying theory are given and there are no literature references. These omissions can make no difference to the adequacy of the methods, but it is annoying when one finds in the description of a familiar method the inclusion of an extra reagent with no explanation of its usefulness. I have always disliked being confronted with methods issued by any standardising authority whatsoever, when they give no references and no explanation. No doubt the standardising bodies are of the highest competence; no doubt the methods are of impeccable ancestry, but the sceptical chemist rightly regards them without enthusiasm. He wants to know where they came from before they got into the shop window where they now are.

Apart from this, the setting out of the whole publication is excellent, though the binding will not last long in laboratory use. Five of the methods are spectrographic, and include the analysis of calcium, thorium and uranyl nitrate for impurities, and the determination of beryllium in atmospheric dust. There are eighteen spectrophotometric methods, some of which are most interesting, *e.g.*, the determination of carbon in uranium by converting it to carbon disulphide, which is finally measured as the familiar cupric diethyldithiocarbamate. The determination of cobalt, scandium, iron, beryllium and other elements by radioactivation is fully described. There are also methods for analysing silicate rocks, refractories, etc., for twelve constituents. The procedures are not those in common use in this country; extended trial would be necessary to establish what advantages they have. Few inorganic analysts will be unable to find something interesting in this collection, which also indexes the hundred methods previously issued. H. N. WILSON

ZONENSCHMELZEN. By Professor Dr. HERMANN SCHILDKNECHT. Pp. xii + 226. Weinheim: Verlag Chemie G.m.b.H. 1964. Price DM 26.

In 1961 Professor Schildknecht announced (*Chem. Ing. Techn.*, 1961, **33**, 352) that he was preparing a monograph on zone melting. This is the volume that has now appeared and it is, as Dr. Pfann remarks in a dedication, the first book in the German language to give a comprehensive treatment of the subject. The zone melting of all types of material is discussed, but in 226 pages it naturally has not been possible to present all the information in the two extant monographs on the zone melting of elements and inorganic compounds and the monograph devoted to the treatment of organic compounds. However, as was to be expected from Professor Schildknecht's interests, the book is particularly strong in the description of techniques for treating small amounts of fairly low-melting organic compounds.

The theoretical section is noteworthy for the thirteen pages devoted to ternary systems, considered in terms of "Rüchstandlinien," a treatment reminiscent of that favoured by the Dutch school in the theory of distillation. Such a study of zone melting is useful for the clarification of thought, but the method is little used elsewhere in the book.

The section on apparatus, which has some excellent diagrams and photographs, differs from those found in the other treatises because of the emphasis it places on the use of alternate heaters and coolers. More than a dozen drawings and photographs show arrangements of such elements. Space is also given to photographs and drawings of the ingenious, but rather complicated, equipment for ring-zone melting.

A third section of the book (59 pages) contains two parts, reporting results of the zone melting of elements and inorganic compounds, and of organic compounds. Naturally, these parts cannot be comprehensive because of their small size, and therefore any criticism of omission must depend on the interests of the reader. Nevertheless, I must admit my personal disappointment that neither here, nor elsewhere in the book, is any mention made of Beynon and Sauders' paper "Purification of Organic Materials by Zone Refining," *Brit. J. Appl. Phys.*, 1960, **11**, 128, which reports many observations made in the Imperical Chemical Industries Dyestuffs Division.

Analysts requiring information on the zone melting of long-chain alcohols and of small samples of organic compounds will find in this book a valuable survey of the work of the Schildknecht school, but English-speaking readers will probably prefer other texts for accounts of procedure and equipment.

E. F. G. HERINGTON

SPECTROSCOPY AND PHOTOCHEMISTRY OF URANYL COMPOUNDS. By EUGENE RABINOWITCH and R. LINN BELFORD. Pp. x + 368. Oxford, London, Edinburgh, New York, Paris and Frankfurt: Pergamon Press. 1964. Price 80s.

"The Chemistry of Uranium," by J. J. Katz and E. Rabinowitch, which was based on information assembled during the wartime Manhattan Project is well known to many chemists, particularly those working in the field of nuclear energy. A second volume, which was to have covered uranyl compounds was never completed, but the section dealing with spectroscopy has been expanded to include later work and is now published by Pergamon as Volume 1 in the International Series of Monographs on Nuclear Energy–Chemistry Division.

The authors of this present volume state that their aim was to provide a comprehensive guide to past work, since in their opinion, many research workers make inadequate use of previously reported results. This objective has been very largely achieved in a book that is based on the data and conclusions abstracted from well over 300 original papers that date from 1833 to 1961. It is admitted that the literature coverage from 1960 onwards is sparse, and in a book of this type it is inevitable that certain sections will be soon out-dated. The addition, by the reader, of notes on later work is, however, facilitated by the chronological arrangement within each section.

Chapters 1, 2 and 4 are of approximately equal length with about 90 pages each, whereas Chapter 3 is half this length. The final Chapter 5 contains 15 pages, which are followed by a complete bibliography, author index and subject index.

Chapter 1 covers the infrared, visible and fluorescence spectra of uranyl salts in the solid state with a separate section on the interpretation of spectra.

The second chapter begins with an account of the effect of the hydrolysis of uranyl salts on absorption and fluorescence, and goes on to describe the spectra of the uranyl ion when complexed with inorganic and the simpler organic acids. Thirty pages are devoted to absorption and fluorescence spectra in a wide variety of organic solvents, and the chapter is concluded with a description of Raman and infrared spectra of uranyl salt solutions.

A theoretical interpretation of slowly decaying fluorescence prefaces the third chapter, which then details the intensity and decay of fluorescence of uranyl compounds in crystal form and in solution.

The photochemical reactions of uranyl salts with inorganic reductants, alcohols and aliphatic, aromatic, hydroxy, thio- and keto- acids constitute the fourth chapter, and the final 15 pages of the text contain a theoretical appraisal of the electronic structure of the uranyl ion and the interpretation of the near-visible spectra.

The whole book has a theoretical bias and is not concerned with the experimental techniques that have been used to produce the data presented. As would be expected, differences of both results and interpretations are reported, and it is felt that a more critical assessment of results *vis-à-vis* the experimental conditions used, would have been useful.

The overall subject matter of this publication is relatively narrow, and consequently the individual aspects are presented in considerable detail. However, the following well known phenomena relating to uranium compounds are either not described or receive scant attention. No mention is made of the intense fluorescence produced by uranic compounds in a fused sodium fluoride matrix, which is widely used in the determination of sub-microgram amounts of uranium. Similarly, the absorption spectra of the many organic complexes that have been used in the quantitative determination of low concentrations of uranium are apparently deliberately omitted. Again the absorption spectra of the uranyl nitrate - alkyl phosphate complexes, which have played such an important role in the recovery and purification of uranium, are represented by a single spectrum, which is not discussed in the text.

The whole book is written in an easy, lucid style and represents an immense amount of information in a readily accessible, concentrated form, completely free from extraneous padding. The high quality of the diagrams, which are generally clear and well annotated, is marred only by page 39, where eighteen infrared spectra are crowded into three-quarters of a page.

The correct form of most of the printer's errors is self evident. However, the reference to the fluorescence of potassium sulphate, the table on page 142 which does not substantiate the conclusions drawn in the text, and the solution of uranic oxide in tartaric acid (page 314), which

produces a residue containing "an undetermined Cu^{++} reducing compound" lead to a number of possible speculations.

It is felt that this volume is unlikely to appeal directly to the practical analyst, since analytical applications of the spectroscopic features of uranium compounds appear to be intentionally excluded. In addition, the experimental techniques used to obtain the results presented have not been described. Research workers will, however, find this book invaluable not only for its presentation of past work, but also for the indications of those fields in which data are incomplete or where either new approaches or more refined techniques are required. A. E. SAWYER

ATLAS AND TABLES FOR EMISSION SPECTROGRAPHIC ANALYSIS OF RARE EARTH ELEMENTS. By CH. KEREKES. Edited by L. LÁNG. Tables, pp. ii + 16 Tables: Atlas, 12 Spectrographic charts. Oxford, London, Edinburgh, New York, Paris and Frankfurt: Pergamon Press. 1964. Price 100s.

The book consists of the following—

(*i*) A set of tables in which scandium, yttrium, lanthanum and each of the thirteen stable rare-earth elements are listed in order of atomic number, together with their analysis lines given in order of increasing frequency (although listing is given in terms of wavelength) and the relative intensity of each line. Listed with each element are the interfering lines for the other fifteen elements of this series, present in the spectral pure-grade rare-earth oxides (*ex* Johnson, Matthey & Co.) that were used in the composition of these tables.

(*ii*) An atlas composed of twelve reproductions of the photographic plate from 5600 to 2600 Å, with all the possible lines being labelled, with a background of an iron spectrum photographed on a Zeiss Q24 spectrograph. The magnification of the atlas corresponds to a factor of 20 of the original Agfa plate, although the actual size of plate is not given.

(*iii*) A short introduction to the tables and atlas in four languages, English, German, French and Spanish. The introduction explains how to use them, together with setting out the technical details of the operating conditions which were used.

Although this book is expensive, for those who are engaged in investigations on the rare-earth elements it represents a condensed précis of the conditions necessary for their spectrochemical analysis. G. NICKLESS

ADVANCES IN X-RAY ANALYSIS. Volume 7. Edited by WILLIAM M. MUELLER, GAVIN MALLETT and MARIE FAY. Pp. x + 662. New York: Plenum Press. 1964. Price $22.50.

This is not a textbook. The volume is the vehicle for publication of the papers that were presented at a Conference on Applications of X-Ray Analysis held at Denver in August, 1963. This conference was the twelfth of an annual series and the present volume is the seventh in which the proceedings are, or have been, published. The declared aim of the publications is to present "within the shortest possible time after completion the results of research and new developments in the application of X-rays to the solution of physical and chemical problems."

Three rather different fields of application of X-rays are covered by the papers included in this book. About half the book, extending over 27 papers and 317 pages, is concerned with X-ray diffraction. The remainder deals with elemental analysis by X-ray spectroscopy, but this topic can be sub-divided into analysis by the electron-microprobe technique on the one hand, and macro-scale X-ray spectroscopy on the other. After the eight papers on electron-microprobe analysis, there is a report of a panel discussion on the subject matter covered in these papers. A comparatively short paper immediately following the section on X-ray diffraction does not fall within any of the categories mentioned, but discusses a new approach to elemental analysis by X-ray absorption.

In the X-ray diffraction part of the book, there are papers on techniques and devices, as well as papers describing applications. For example, new approaches to the indexing of X-ray diffraction patterns are described, the separation between contributions of small particle size and lattice strain to line broadening is discussed, and the influence of various angular measures of diffractometer line profiles on lattice-parameter evaluation is considered. In the sphere of more direct applications, one finds papers on a technique for determining low percentages of retained austenite in steels, on preferred orientation associated with forming and fabrication of ceramic materials, on structural aspects of the precipitation of magnesium fluoride in lithium fluoride crystals and about the study of an amalgamation process for preparation of pre-alloyed iron - nickel powders, to mention only a few.

The analyst will probably be most interested in the papers in the second half of the book. Such titles as "Limitations of the Linear Intensity - Concentration Approximation in Electron Probe Microanalysis," "Instrumental Developments for Electron Microprobe Readout," and "Methods of Quantitative Electron Probe Analysis," provide an indication of the kind of topics included in the section about the microprobe technique.

There are sixteen papers dealing with various aspects of X-ray spectroscopic analysis. Guidance to the variety of topics covered is given by the following rather arbitrary selection of titles—

(*a*) X-ray Fluorescence Analysis for Sodium, Fluorine, Oxygen, Nitrogen, Carbon and Boron.
(*b*) Evaluation of a Demountable X-ray Tube Vacuum Spectrograph for the Determination of Low-Atomic-Number Elements.
(*c*) The Accurate Determination of Major Constituents in the Presence of Interelement Effects.
(*d*) X-ray Spectrometric Determinations of Composition and Distribution of Sublimates in Receiving-Type Electron Tubes.
(*e*) Improved Trace Analysis with the Use of Synchronised Electronic Discrimination in an X-ray Scanning Procedure.
(*f*) Performance of an Unattended Automated X-ray Spectrograph.

The penultimate paper is of particular interest, since it describes an attempt at developing a dual-function diffractometer - spectrometer. The instrument is a logical follow-up of a dual-function neutron diffraction - X-ray diffraction equipment that was described in a paper in an earlier volume of the Advances in X-ray Analysis series. Facilities for both X-ray diffraction and X-ray fluorescence spectroscopy are provided on the same basic unit, and it is claimed that the change-over from one technique to the other can be made in a matter of seconds.

To consider this volume in complete isolation from the earlier numbers in the series is questionable. During the period marked by the publication of all seven volumes of the series, there has been remarkable progress in the fields of X-ray diffraction and X-ray spectroscopy, and it is through a study of the papers as a whole that the status of the present volume can be seen in true perspective. It is undoubtedly a worthy successor to Volume 6, and includes many instructive accounts of the most recent developments in applied X-ray analysis. The one serious criticism is that nearly all the contributions are of American origin, and consequently the volume is less representative of world progress than were previous volumes. It is, nevertheless, to be warmly recommended as important reading to any analyst who is closely, or even more remotely, concerned with the potentialities of modern instrumental techniques, particularly X-ray spectroscopy.

H. P. Rooksby

Manuel pratique de Chromatographie en Phase Gazeuse. Edited by Jean Tranchant. Pp. ii + 231. Paris: Masson et Cie. 1964. Price 36 F.

This small book, in the French language, contains an introduction by the editor and eight chapters, two of which are written by the editor, the others by seven collaborators. The introduction performs the useful task of setting out the place of gas chromatography in relation to other chromatographic techniques. It includes a bibliography of important books on the subject and a list of nomenclature and symbols is also provided.

Chapter 1 is concerned with principles and theory. It gives the terminology of gas chromatography, together with a schematic description. The theoretical treatment is kept simple, as is necessary when compressing such a large field into only 17 pages. However, distribution isotherms and their effect on peak shape are discussed, plate theory is considered, the Van Deemter equation is introduced and the interpretation and application of Van Deemter curves are considered. The particular problems of gas - solid chromatography are outlined and the value of frontal analysis in this field emphasised. Displacement analysis is mentioned. Finally, three applications of theory are quoted as examples.

Apparatus for gas chromatography is considered, section by section, in Chapter 2 and is illustrated by good diagrams and photographs. This is followed by a detailed treatment of columns and accessories in Chapter 3 and of detectors in Chapter 4. In the former the crucial importance of correct column conditions is stressed and much information is provided concerning the choice of stationary phase. The coverage is wide and includes packed columns, capillary columns, preparative and counter-current columns. The advantages and disadvantages of gas - solid chromatography are considered and an up-to-date treatment of modern gas - solid columns, including capillary columns, is given. The account of available detectors is perhaps too complete,

since a number that are unimportant and of little application are included. Classification is by sensitivity, which has some drawbacks, but there is a useful table summarising the properties of the principal detectors. The general characteristics required of a detector are clearly stated and the factors affecting sensitivity are outlined. The descriptions are generally good, especially that of the gas-density balance.

Chapters 5 and 6 are concerned with qualitative and quantitative analysis. The basic considerations are outlined satisfactorily, with just sufficient theory to facilitate understanding. The effect of the polarity of the stationary phase is dealt with and the choice of stationary phase considered. The use of retention data is discussed and both chromatographic and other methods of qualitative detections (mass spectrometry, ultraviolet, etc.) are described. The relation between the response of the detector and quantity of substance is discussed and methods of measuring the area of the peak are described. The use of the French word "surface" for area is a little surprising, but it is assumed that this is common usage. The determination of absolute coefficients of proportionality and the measurement of relative coefficients of proportionality are dealt with, and the case of incompletely separated peaks receives attention. Choice of the method of standardisation is outlined and the "internal-standard method" given due importance. Precision and reproducibility are discussed and the problems of trace analysis considered.

Temperature-programmed gas chromatography is dealt with in Chapter 7, showing that the book is abreast of the latest developments. Elements of the theory are given, together with practical considerations and examples of use.

Chapter 8 is devoted entirely to applications and large numbers of compounds are considered in groups. The majority are organic species, but permanent gases, aqueous solutions, biochemical systems, perfumes and air pollution also receive attention. This chapter and the whole book is copiously supplied with references. Altogether about 660 are listed, covering the world literature up to late 1963. The index is surprisingly good for a volume of this size and type. There is overlap between chapters in a number of places, but this is probably unavoidable and does not seriously detract from the book.

The editor states in the introduction that the purpose was not to write another heavy book on gas chromatography, but instead to produce a small, essentially practical treatise which would save the novice much waste of time in the resolution of purely experimental problems. In this the authors have succeeded in so far as such an objective can be achieved. They have also produced a book that is sufficiently complete to satisfy the requirements of non-specialists who require a general knowledge of the principles and applications of the technique. It is recommended to all who have sufficient grasp of French to understand the clear and relatively simple text. An English translation of this book would be very popular. G. F. REYNOLDS

BIOMEDICAL APPLICATIONS OF GAS CHROMATOGRAPHY. Edited by HERMAN A. SZYMANSKI. Pp. iv + 324. New York: Plenum Press. 1964. Price $12.50.

The introduction and advance of gas chromatography in the biological sciences have been so rapid that it is difficult to appreciate the state of the art, but this volume provides a wide and tolerably up-to-date survey, being derived from lectures given at what is termed an "Annual Gas Chromatography Institute" in 1963.

The introductory chapter does not attempt to deal with gas-chromatography theory, but gives useful definitions, formulae required in practice and technical hints. Subsequent chapters by various authors deal with the analysis of amines, alkaloids, amino-acids, steroids, bile acids, carbohydrates, fatty acids and volatile anaesthetics. Thus, with the exception of respiratory-gas analysis, most current biomedical applications are dealt with.

The general style is straightforward with emphasis on the practical applications of the techniques; specific biological investigations are not reported. There is extensive discussion on the selection of phases and numerous tables of chromatographic constants for various compounds. The bibliographies are comprehensive.

The standard reached by the different authors is uneven, but the chapter on steroids by Vanden Heuvel and Horning is particularly good and deals at length with the problems of identification and quantitative analysis. There are many illustrative chromatograms in the book and they look un-retouched, which is more than can be said about some publications on this subject.

Perhaps the most serious fault is the lack of an index, but there are other omissions as well. One of the major problems facing anyone wishing to use these techniques is in deciding which type of apparatus to buy. Sound advice is hard to come by, and unfortunately the authors deal

briefly or not at all with topics such as the relative merits of different detectors for various applications.

However, as a reference book it can be recommended to anyone considering the use of gas chromatography in biomedical work, and might well encourage present users to attempt other applications.

R. F. FLETCHER

GUIDE TO ACTIVATION ANALYSIS. Edited by WILLIAM S. LYON, Jr. Pp. xx + 186. Princeton (New Jersey), Toronto, New York and London: D. Van Nostrand Company, Inc. 1964. Price 46s. 6d.

This book was prepared under the auspices of the United States Atomic Energy Commission, and as such must be considered a work of some authority. However, it does not live up to the claim made for it that it is suitable for both the "neophyte" and the "sophisticate"—indeed, it is doubtful if any book with 150 pages of text could—and it tends to suffer from the attempt to do so.

The balance of the chapters makes it of relatively little use to the analyst trying to decide whether activation analysis is worth investigating. For example, 27 pages are given to the use of γ-ray spectrometry, including such complexities as spectrum stripping and the use of computers, whereas radiochemical separation techniques, which are surely the method of choice for an analyst during the exploratory stages, are dismissed in six rather superficial pages.

The examples chosen in Chapter 8 are also less informative than they might be. They are designed to reveal the pitfalls in the method, but newcomers to the field might well appreciate at least one strightforward application to show the technique at its simplest.

Similarly, the sections on counting techniques are not very informative for a beginner. No mention is made of the use of a Geiger - Müller counter for solution counting, despite the many advantages of this approach, whereas the whole complex business of scintillation counting of liquids is dismissed in one paragraph.

Another major criticism of the book is the attitude to radiation safety shown in Appendix B. Work with radioactive materials is already hampered by an unjustified view of its dangers, without a book of this kind exaggerating them further. Figure B1 shows 10-μC amounts of phosphorus-32 being handled with beaker tongs. This is quite unnecessary. Even worse is Figure 2, which shows 10 μC of iodine-131 surrounded with an utterly nonsensical amount of lead shielding. Either $\frac{1}{8}$-inch of lead or 1 foot of distance would reduce the dose from a bottle containing 10 μC of iodine-131 to a level that a radiation worker could tolerate night and day permanently without exceeding the maximum permissible level. Care in working with radioactive materials is obviously essential, but the care demanded must bear some relationship to the risks involved. The application of over-rigorous precautions will only bring the whole concept of radiological protection into disrepute.

Despite these criticisms, this book does have a useful place. There is much valuable information collected together, particularly in the tables and the figures, and the mass of data in Appendix A on the application of activation analysis should prove a good source of reference.

The book is well produced and on the whole free from printing errors. It should form a useful addition to a library containing other books on radiochemistry and activation analysis.

T. T. GORSUCH

THE CHEMISTRY OF NATURAL PRODUCTS 3. Special Lectures presented at the Third International Symposium on The Chemistry of Natural Products held in Kyoto, Japan, 12–18 April, 1964. International Union of Pure and Applied Chemistry. Pp. viii + 191. London: Butterworth & Co. (Publishers) Ltd. 1964. Price 60s.

Butterworths are the official publishers to the International Union of Pure and Applied Chemistry. The text of this volume is directly reprinted from *Pure and Applied Chemistry*, 1964, 9, 1–191, and its binding is uniform with this publisher's series of Proceedings of Conferences of I.U.P.A.C. There are three papers of interest to analysts, "High Resolution Mass Spectrometry of Natural Products," by K. Biemann (U.S.A.); "Isotope Labelling and Mass Spectrometry of Natural Products," by C. Djerassi (U.S.A.); "Recent Advances in X-Ray Analysis of Natural Product Structures," by J. Monteath Robinson (U.K.).

This type of dual publication makes it possible, at very little extra cost, to satisfy the desires of authors to have their papers "in the literature," and also the desires of delegates (and others) for a compact account of the Conference.

EDITOR

REPORTS OF THE ANALYTICAL METHODS COMMITTEE OBTAINABLE FROM THE SECRETARY

The Reports of the Analytical Methods Committee listed below may be obtained direct from the Secretary, The Society for Analytical Chemistry, 14 Belgrave Square, London, S.W.1 (not through Trade Agents), at the price of 1s. 6d. to members of the Society and 2s. 6d. to non-members. Remittances must accompany orders and be made payable to "Society for Analytical Chemistry."

Certain Reports published before 1946 have been omitted from this list, but are still available.

Additives in Animal Feeding Stuffs Sub-Committee:

Report of the Antibiotics Panel: The Determination of Penicillin, Chlortetracycline and Oxytetracycline in Diet Supplements and Compound Feeding Stuffs.

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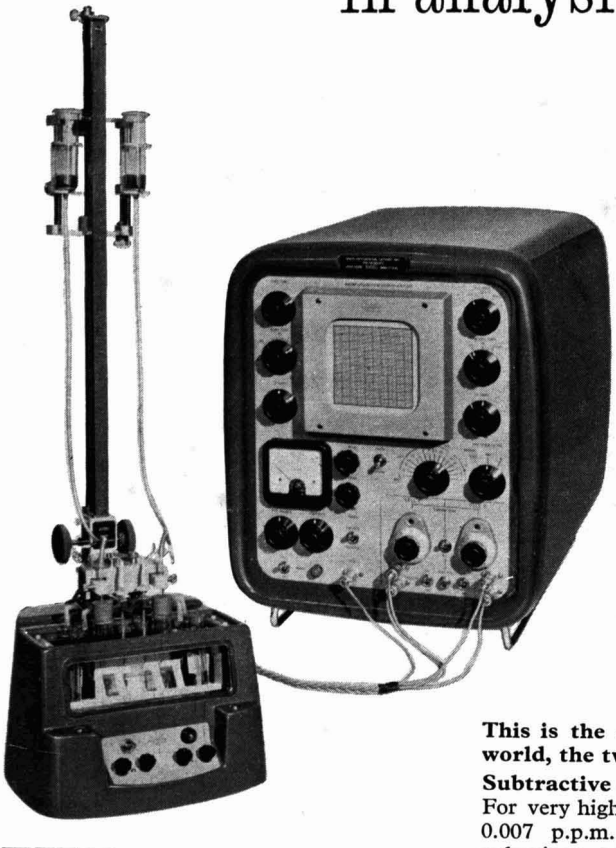
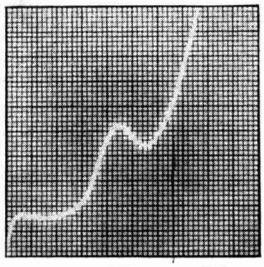
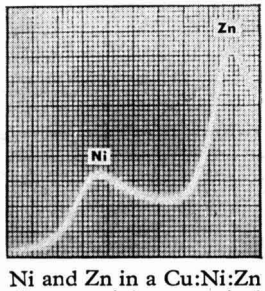




0.04 ug/ml Zn in a pH 4.6 buffer. Full compensation for cell capacity and base line slope.



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Ne	**Na**	**Mg**	**Al**	**Si**	P	**S**	Cl	
Ar	**K**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe Co Ni**
	Cu	**Zn**	**Ga**	**Ge**	**As**	**Se**	Br	
Kr	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	Tc	**Ru Rh Pd**
	Ag	**Cd**	**In**	**Sn**	**Sb**	**Te**	I	
Xe	**Cs**	**Ba**	**La Ce Pr Nd** Pm	**Sm Eu Gd Tb**				
	Dy Ho Er Tm Yb Lu			**Hf**	**Ta**	**W**	**Re**	**Os Ir Pt**
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Rn	Fr	Ra	Ac	**Th**	Pa	**U**		

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