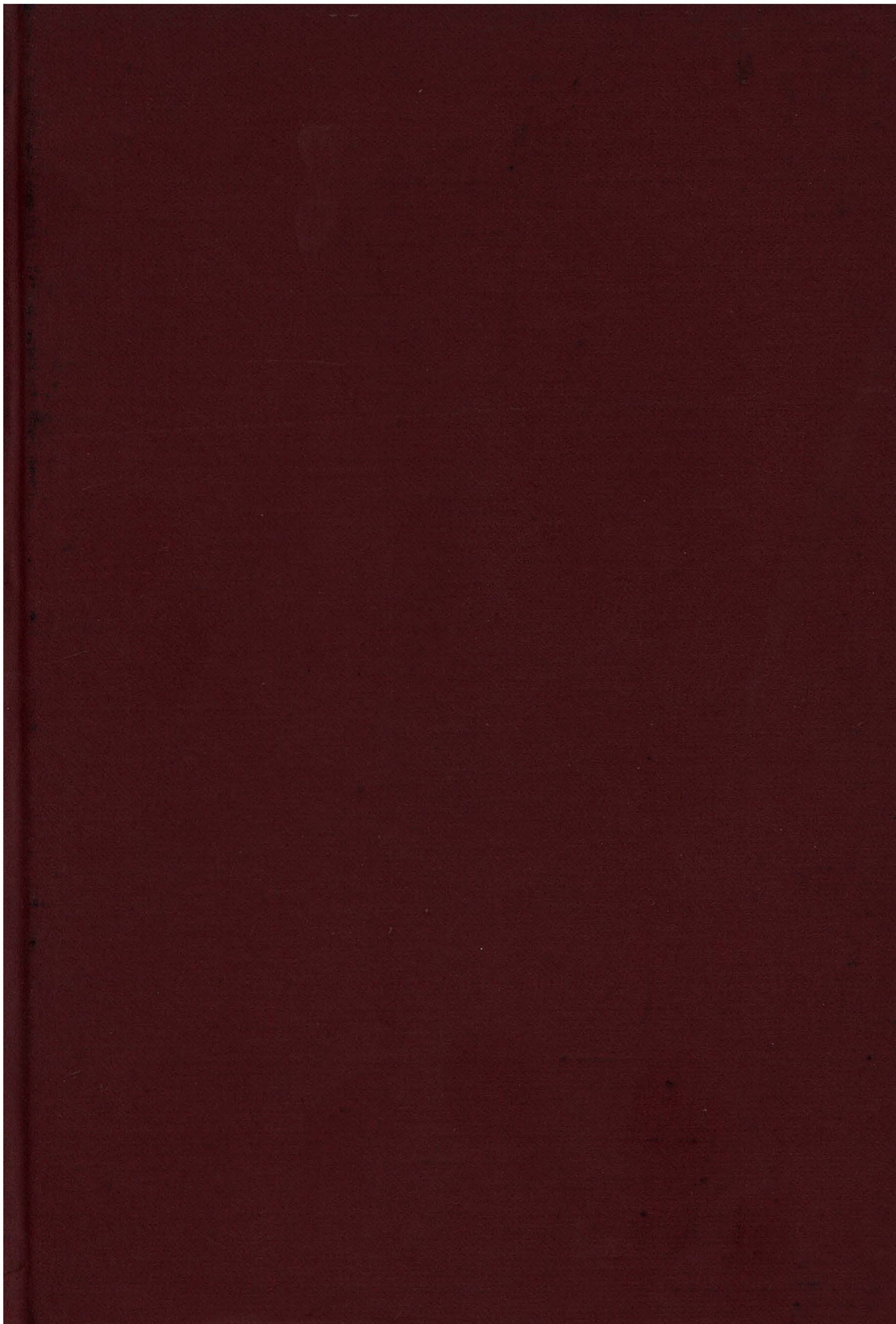

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Zirconium mandelate: Thermogravimetric study of mandelates of zirconium and hafnium. Adams and Holness, 603.
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ERRATA:

VOL. **85**, 1960:

p. 176, 1st line under "PROCEDURE FOR LARGE QUANTITIES OF SILVER." *For* "stage 4" *read* "stage 9."

VOL. **88**, 1963:

p. 967, "Method." *After the last reagent* (Tris glycerol buffer), *add the following paragraph*—

"*Combined reagent*—Dissolve 10 mg of glucose oxidase, 1 mg of horseradish peroxidase and 10 mg of *o*-dianisidine hydrochloride in 100 ml of tris glycerol buffer."

p. 967, 1st line of "Procedure." *Before* "reagent" *insert* "Combined."

p. 967, 4th line of "Procedure." *After* "2 mg" *insert* "per ml."

VOL. **89**, 1964:

p. 1, 15th line. *For* "to test both" *read* "both to test."

p. 4, 9th line from foot of page. *For* "calcium DL-pantothenate" *read* "calcium D-pantothenate."

p. 5, 3rd line from foot of page. *For* "pH 6 to 8" *read* "pH 6·8."

p. 19, equation (4.4). Insert a rule between the numerator and denominator in right-hand brackets.

p. 20, equation (7.2), denominator of the fraction in the centre brackets. *For* "$\overline{N}$" *read* "$\overline{N}w$."

p. 21, 12th line reference at end of line. *For* "2" *read* "4."

p. 25, 3rd line from foot of page. *For* "functions" *read* "fractions."

p. 30, reference 2. *For* "670" (the page number of the reference) *read* "81."

p. 30, reference 4. *For* "81" (the page number of the reference) *read* "682."

p. 78, 11th line. *For* "L. S. Theobold" *read* "L. S. Theobald."

p. 80. Review of BRITISH PHARMACOPOEIA 1963.

An inadvertent transposition led to the inclusion in this Review of a statement that biological assay was used for thyroid. Thyroid is in fact assayed by an oxygen-flask method. The fourth paragraph of the Review should be amended to read—

"It is interesting to note that in some instances (benzylpenicillin, benzathine penicillin and procaine penicillin) it has been possible to replace biological assay with chemical tests and assays."

p. 121, reference 6. This should read "Merck Index, Sixth Edition, Merck & Co. Inc., Rahway, N.J., U.S.A., 1952, p. 895."

p. 189, 2nd line below expression defining D. *For* "i" *read* "i_1."

p. 189, 10th line from foot of page. *For* "i" *read* "i_1."

p. 189, 11th line from foot of page. *For* "$v_1 = wD + i$" *read* "$v_1 = wD + i_1$."

p. 233, 1st line under "Procedure." *For* "(10 ml)" *read* "(100 ml)."

p. 243, reference in 1st line of 1st footnote. *For* "7" *read* "8."

p. 244, equation (2). *For* "$(E^0{}_2 - E^0{}_2)$" *read* "$(E^0{}_2 - E^0{}_1)$."

p. 245, heading to Table II. *For* "E_{0Ag}" *read* "$E^0{}_{Ag}$"

p. 245, 11th equation in Table II, right-hand side. *For* "$H_2TeO_3 + 3H_2O$" *read* "$H_2TeO_3 + H_2O$."

p. 248, 3rd line from foot of page. *For* "and" *read* "but."

p. 260, reference 3. *For* "Quantitative" *read* "Qualitative."

p. 270, 7th line from foot of page. *For* "ratios to calcium" *read* "ratios of calcium."

p. 280, 14th line. *For* "530 mμ" *read* "520 mμ."

facing p. 289, Legend to Fig. 1. *For* "Paper" *read* "Thin-layer."

p. 364, Legend to Fig. 1. *For* "V_1 = VA26T stabiliser" *read* "V_1 = VA26T photoelectric cell."

p. 489, last line of page. *For* "chrome - alumel" *read* "chromel - alumel."

p. 489, 3rd line from foot of page. *For* "18 × 9 inches" *read* "18 × 9 × 9 inches."

p. 490, 2nd line. *For* "slightly into the furnace" *read* "into the centre of the furnace."

p. 490, 3rd line. *For* "are" *read* "were."

p. 490, 6th line under "REAGENTS." *For* "pH 5·5" *read* "pH 5·0."

p. 492, Table V, heading to 5th column. *For* "open-tube" *read* "sealed-tube."

p. 494, 7th line. *For* "Dr. I. J. M. Muir" *read* "Dr. I. H. M. Muir."

p. 521, 3rd table of analytical results. *For* "$C_3H_5NO_3$" *read* "$C_3H_7NO_3$."

p. 554, 10th line. *Delete* "1- and."

p. 689, 3rd line under "REPORT." *After* "this" *insert* "form."

p. 699, 25th line. *For* "pyrethrum II" *read* "pyrethrin II."

p. 708, 1st table of analytical results. *For* "C_5HNOS_5" *read* "C_5H_5NOS."

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THE ANALYST

Analytical Methods Committee

Report of the Additives in Animal Feeding Stuffs Sub-Committee

PART 4.* REPORT OF THE VITAMINS (WATER-SOLUBLE) PANEL

The Determination of Water-soluble Vitamins in Compound Feeding Stuffs

INTRODUCTION

THE Vitamins (Water-soluble) Panel was set up under the Chairmanship of Dr. A. J. Amos, and its membership was: Dr. J. E. Ford, Mr. B. M. Gibbs, Mr. S. A. Price, Mr. H. Pritchard, Mr. F. Clermont Scott, Mr. G. Sykes, Mr. S. Varsanyi and Dr. J. Williams, with Dr. C. H. Tinker as Secretary; Dr. F. W. Norris joined the Panel for investigations into the determination of riboflavin. The Panel was appointed to ascertain whether or not methods could be recommended that would permit compound feeding stuffs to be assayed for choline, nicotinic acid, pantothenic acid, riboflavin, vitamin B_6, vitamin B_{12} and vitamin K (2 methylnaphthaquinone derivatives).

Most of the water-soluble vitamins used as supplements in animal feeding stuffs occur naturally in many of the materials commonly used as ingredients of animal rations. Usually, therefore, the result of a vitamin assay will represent the total amount of the vitamin in the foodstuff and will be no guide to the amount, if any, present as a supplement. Further, even the total vitamin content revealed by a microbiological assay will not necessarily be a measure of the biological value of the feeding stuff as a source of the vitamin in question, because some vitamins may exist in bound forms that are not necessarily equally available both to test organisms and animals.

The possibility of mal-distribution of an added vitamin, and the heterogeneous nature of most animal rations, demand that the sample received by an analyst shall be ground finely, mixed well, and carefully sub-divided by him if the relatively small amount used for an assay is to be representative of the parent sample. Even when these precautions are taken, the vitamin content as reported may not be applicable to the bulk from which the analyst's parent sample is drawn. Whether it is or not will depend on the uniformity of distribution of the supplement throughout the bulk, and this is a matter over which the analyst has no control, and indeed about which he may have no knowledge.

The reproducibilities reported by the Panel are based on results obtained in laboratories versed in microbiological assays. The results of assays made in laboratories not experienced in this specialised field are likely to differ more widely.

As a result of its collaborative investigations, which have in the main involved microbiological procedures because of their greater sensitivity and specificity, the Panel is able to recommend methods for determining nicotinic acid, pantothenic acid, riboflavin and vitamin B_{12} in compound feeding stuffs, but has to report that existing procedures for determining choline and vitamin B_6 have failed to give results of acceptable precision when applied to such feeding stuffs. Various attempts to modify methods for these last two vitamins so as to make them suitable for use with compound feeding stuffs have proved unsuccessful, and in the opinion of the Panel the solution of the problem calls for more fundamental investigations, which could well become long-term research projects. In the Panel's opinion, a suitable method for determining vitamin K in compound feeding stuffs is not available.

*Part 1 appeared in *The Analyst*, 1963, **88**, 835, and Parts 2 and 3 in *The Analyst*, 1963, **88**, 925 and 935.

The methods studied by the Panel for determining nicotinic acid, riboflavin and vitamin B_{12} were those recommended previously by panels of other sub-committees of the Analytical Methods Committee for assaying foods; it was gratifying to find that the collaborative tests established that the applicability of the methods could be extended to include animal feeding stuffs.

RESULTS AND RECOMMENDATIONS

NICOTINIC ACID—

The method selected for collaborative study was the microbiological procedure, in which *Lactobacillus plantarum* (*L. arabinosus*) is used, previously investigated by the Analytical Methods Committee[1] for assaying foods. Five samples of compound feeding stuffs were assayed in each of six laboratories; some samples were unsupplemented and others contained some or all of the following additives: vitamins, amino-acids, trace metals, and a coccidiostat or an antibiotic. The results revealed that if several laboratories, versed in microbiological assays of this type, analyse samples of the same compound feeding stuff containing 15 to 90 µg of nicotinic acid per g by the method previously recommended by the Analytical Methods Committee, the results may be expected to lie within ±20 per cent. of the mean.

The method is therefore recommended for the determination of nicotinic acid in compound feeding stuffs.

PANTOTHENIC ACID—

Pantothenic acid is widely distributed in natural products and may also be added, commonly in the form of the DL calcium salt, to ensure that the vitamin is present at an adequate level in compound feeding stuffs for livestock.

Naturally occurring pantothenic acid may occur both in the "free" form and in forms unavailable to the test organism, *e.g.*, as coenzyme A. Hence microbiological assays involving simple extraction methods take no account of the "bound" vitamin, and so are liable to give an underestimate of the total pantothenic acid content, especially with some types of sample. During a preliminary collaborative test the Panel found, for example, that whereas a simple extraction in the cold with a phosphate buffer at pH 6·6 resulted in virtually complete extraction of pantothenic acid from a sample of chick mash, this procedure was inadequate to release the vitamin from a sample of dried yeast. Since the proportion of dried yeast, or of other constituents containing bound forms of pantothenic acid, may vary in samples of compound feeding stuffs, it is clear that extraction with phosphate buffer cannot invariably be relied on in measuring the total pantothenic acid content of a compound feeding stuff.

Several enzymic procedures have been proposed from time to time for liberating pantothenic acid from its bound forms, notably those in which mylase-P, takadiastase and papain is used, but it was shown by Novelli, Kaplan and Lipmann[2] that the pantothenic acid bound in coenzyme A was released quantitatively only by a dual-enzyme system involving both intestinal phosphatase and a chicken- or pigeon-liver extract. These enzymes may themselves contain appreciable amounts of pantothenic acid, and a blank determination must therefore be carried out simultaneously with samples to be assayed. This, in turn, introduces an additional source of error into the determination. In the opinion of the Panel, however, it is preferable to determine the *total* pantothenic acid—in spite of the relatively low precision associated with such assays—rather than to measure more precisely only the *free* pantothenic acid. Nevertheless, the Panel is aware of the fact that with some samples the complications of the enzymic hydrolysis procedure could, with justification, be omitted with a concomitant gain in precision.

The method selected for collaborative study was based on the microbiological method in which *Lactobacillus plantarum* (*L. arabinosus*) is used, published by the United States Department of Agriculture.[3] Six samples, including unsupplemented and supplemented animal feeding stuffs and dried yeast, were assayed in each of seven laboratories. The results obtained revealed that if several laboratories, versed in microbiological assays of this type, analyse samples of the same compound animal feeding stuff containing 10 to 40 µg of pantothenic acid per g by the recommended method, the results may be expected to lie within ±40 per cent. of the mean.

The method recommended by the Panel, therefore, is a method designed to measure *total* pantothenic acid. It is based on the method published by the United States Department of Agriculture,[3] but a medium similar to Barton-Wright's[4] is used. Details of the recommended method are given in Appendix I.

RIBOFLAVIN—

At an early stage of the Panel's investigations it was established that the riboflavin activity for *Lactobacillus helveticus* of an extract of compound feeding stuff circulated to Panel members could be determined by the participating laboratories with an acceptable "between laboratories" variance by the microbiological procedure previously recommended by the Analytical Methods Committee[1] for assaying foods. However, the results reported when each laboratory made its own extract of a sample of a compound feeding stuff showed unacceptable divergence. Collaborative investigations were accordingly undertaken on the effect of variations in the method of extraction, and the resulting introduction of modifications to the procedure permitted Panel members to determine riboflavin activity in compound feeding stuffs with a precision commensurate with those of the assay methods recommended for the other vitamins in this report. Collaborative studies of a microbiological method in which *Streptococcus zymogenes* is used showed that, despite its greater sensitivity, it had no advantage over that in which *L. helveticus* was used.

In the light of collaborative tests, the Panel is of the opinion that if several laboratories, versed in microbiological assays of this type, analyse samples of the same compound feeding stuff containing 2 to 7 μg of riboflavin per g by the method involving basal medium Y, previously recommended by the Analytical Methods Committee,[1] but preparing and extracting the sample as described in Appendix II of this Report, the results may be expected to lie within ± 35 per cent. of the mean.

This modified method is therefore recommended for the determination of riboflavin in compound feeding stuffs.

VITAMIN B_{12}—

The method selected for collaborative study was the microbiological procedure, in which *Ochromonas malhamensis* is used, previously investigated by the Analytical Methods Committee[5] for assaying foods. Four samples of animal feeding stuffs, two unsupplemented and two supplemented with cyanocobalamin, were assayed in each of six laboratories. The results revealed that if several laboratories, versed in microbiological assays of this type, analyse samples of the same compound feeding stuff containing 20 to 50 mμg of vitamin B_{12} per g by the method previously recommended by the Analytical Methods Committee, the results may be expected to lie within ± 35 per cent. of the mean.

This method is therefore recommended for the determination of vitamin B_{12} in compound feeding stuffs.

Appendix I

RECOMMENDED METHOD FOR THE MICROBIOLOGICAL ASSAY OF PANTOTHENIC ACID IN COMPOUND FEEDING STUFFS

Normal bacteriological procedures and precautions must be adopted in the preparation of cultures, sterilisation of media and glassware and in the assay procedure.

Reference to sterilisation at 115° or 121° C implies the use, in an autoclave, of saturated steam at a pressure of 10 or 15 lb in excess of atmospheric pressure, respectively, whereby the required temperature of 115° or 121° C is attained.

REAGENTS—

All reagents and ingredients should be of analytical-reagent grade if possible.

Yeast extract - dextrose - agar medium—

Agar	7·5 g
Bacto yeast extract	5·0 g
Dextrose	5·0 g
Distilled water	to 500 ml

Mix the ingredients, and dissolve the agar by steaming for 10 minutes. Transfer 10-ml amounts to 1-oz screw-capped bottles, and sterilise at 121° C for 15 minutes.

Photolysed peptone—Dissolve 40 g of Difco Bacto-peptone, obtainable from Baird and Tatlock (London) Ltd., in 250 ml of glass-distilled water, add 20 g of sodium hydroxide

dissolved in 250 ml of distilled water, and sterilise at 121° C for 15 minutes. Cool, and set aside at room temperature in the light for 24 hours, the solution being exposed to strong light (*e.g.*, that from a 100-watt tungsten-filament lamp, 18 inches distant) for at least 12 hours of this period. Neutralise the solution with glacial acetic acid (about 28 ml), add 11·6 g of hydrated sodium acetate, $C_2H_3NaO_2.3H_2O$, dilute to 800 ml with distilled water, and preserve the solution by adding sulphur-free toluene or chloroform. Store in a refrigerator, *i.e.*, below 5° C; under these conditions the solution will normally keep for a fortnight, but discard it sooner if a precipitate forms.

Inorganic salt solution A—Dissolve 25 g each of potassium dihydrogen phosphate and dipotassium hydrogen phosphate in 250 ml of distilled water, and preserve the solution by adding sulphur-free toluene or chloroform. This solution keeps indefinitely.

Inorganic salt solution B—Dissolve 10 g of magnesium sulphate, $MgSO_4.7H_2O$, 0·5 g of manganese sulphate, $MnSO_4.4H_2O$, and 0·1 g of anhydrous ferric chloride, $FeCl_3$, in 250 ml of distilled water, and add 0·25 ml (5 drops) of hydrochloric acid, sp.gr. 1·16 to 1·18, to prevent any precipitation. This solution keeps indefinitely.

Sodium hydroxide, 0·1 N.

Acetic acid, 0·2 N.

Sodium hydrogen carbonate solution—A 0·85 per cent. w/v solution of sodium hydrogen carbonate in distilled water.

Basal medium—

Hydrated sodium acetate, $C_2H_3NaO_2.3H_2O$	22 g	Xanthine	10 mg
Dextrose	20 g	Nicotinic acid	400 μg
Sodium chloride	5 g	Riboflavin	200 μg
Ammonium sulphate	3 g	Aneurin	100 μg
Difco vitamin-free Casamino Acids	2 g	*p*-Aminobenzoic acid	100 μg
Xylose	1 g	Pyridoxin	100 μg
L-Cystine	200 mg	Biotin	0·4 μg
DL-Tryptophan	100 mg	Photolysed peptone	100 ml
Adenine	10 mg	Inorganic salt solution A	5 ml
Guanine	10 mg	Inorganic salt solution B	5 ml
Uracil	10 mg	Distilled water	to 500 ml

Adjust to pH 6.8 with a 15 per cent. w/v solution of sodium hydroxide in distilled water, with bromothymol blue as external indicator. Store in a refrigerator, *i.e.*, below 5° C, for not more than 48 hours.

Intestinal-phosphatase extract—Extract calf intestinal phosphatase (obtainable from Armour & Co. Ltd.) with cold distilled water (1 ml of water per 10 mg of intestinal phosphatase). Prepare freshly each day.

Pigeon-liver extract—Place in a chilled 50-ml centrifuge tube 2 g of pigeon-liver powder (obtainable from L. Light and Co.) and 20 ml of ice-cold 0·02 M potassium hydrogen carbonate, stir the mixture thoroughly with a glass rod, and place the tube in a centrifuge cup in the freezing compartment of a refrigerator for 10 minutes. Spin in a centrifuge of 15 cm radius at 3000 r.p.m. for 5 minutes, and transfer 2-ml portions of the supernatant liquid to small glass tubes. Store in the frozen condition.

Further treatment of this preparation with Dowex resins may be necessary in order to reduce the enzyme blank value; a convenient procedure is described in the United States Department of Agriculture's Handbook.[3]

Strong standard pantothenic acid solution—From pure dry calcium D-pantothenate prepare a solution to contain 108·8 mg of calcium pantothenate in 100 ml of distilled water.

1 ml ≡ 1000 μg of pantothenic acid.

Store this solution in a refrigerator, *i.e.*, below 5° C.

Dilute standard pantothenic acid solution—Dilute the strong standard pantothenic acid solution with distilled water to give a solution containing the equivalent of 0·02 μg of pantothenic acid per ml. Prepare freshly each day.

Sterile saline solution—A 0·9 per cent. w/v solution of sodium chloride in water, sterilised at 115° C for 30 minutes.

ORGANISM—

The micro-organism used in the assay is *Lactobacillus plantarum* NCIB 8014 (formerly *L. arabinosus* 17-5). Maintain it as a stock culture in yeast extract - dextrose - agar stabs, incubating it at 30° C for 24 hours after inoculation, and make fresh stab cultures monthly.

Subculture for inoculum—Forty-eight hours before the assay, inoculate with a portion of the stock culture 10 ml of sterile broth, prepared by adding to 5 ml of basal medium sufficient of a solution to give 0·05 μg of pantothenic acid per ml of the broth and diluting, if necessary, to 10 ml with distilled water. Incubate at 30° C for 24 hours. Make a final subculture by inoculating a further 10 ml of similarly prepared sterile broth with a portion of the first subculture, and again incubate at 30° for 24 hours.

Inoculum—Spin the subculture for inoculum in a centrifuge, and decant the supernatant liquid. Add 10 ml of sterile saline solution to the residue, mix, spin in a centrifuge, and again decant the supernatant liquid. Repeat the washing of the residue with two further 10-ml portions of sterile saline solution, and then suspend the washed residue in 10 ml of sterile saline solution. Dilute 1 ml of this suspension to 100 ml with sterile saline solution, and use one drop of this diluted suspension for inoculating the assay tubes. Prepare a fresh inoculum from the stock culture for each new assay.

PROCEDURE

When carrying out this microbiological assay, normal bacteriological procedures and precautions must be adopted.

PRELIMINARY TREATMENT OF SAMPLE—

Grind the sample to pass a 60-mesh sieve. To 15 g of the ground sample, add 200 ml of distilled water, and mix thoroughly. Heat in flowing steam for 15 minutes, and then homogenise for 3 minutes in a Waring blender. Transfer the suspension quantitatively to a measuring cylinder, and dilute to 300 ml with distilled water. Return the suspension to the blender, and homogenise for 30 seconds.

Transfer replicate 5-ml portions (equivalent to 250 mg of sample) of the homogenate to a series of test-tubes, 18 to 20 mm in internal diameter and 15 to 16 cm in length. To each tube add 0·5 ml of sodium hydrogen carbonate solution, and then 0·5 ml of intestinal-phosphatase extract and 0·1 ml of pigeon-liver extract, mix, and incubate the mixture in a water-bath at 37° C for 4 hours, stirring occasionally. Transfer the contents of the tubes quantitatively to a series of 100-ml measuring cylinders, washing each tube with about 60 ml of distilled water and adding the washings to the corresponding measuring cylinder. Adjust the contents of each cylinder to pH 4·8 with 0·2 N acetic acid, and dilute to 100 ml with distilled water. Filter each suspension through a Whatman No. 42 filter-paper, and dilute each filtrate until it contains about 0·02 μg of pantothenic acid per ml.

PREPARATION OF ENZYME BLANK SOLUTION—

Treat 5 ml of distilled water, instead of 5 ml of the sample homogenate, as described above under "Preliminary Treatment of Sample," beginning at "Transfer replicate 5-ml portions . . . .", but omitting the final dilution of the filtrate.

DETERMINATION OF PANTOTHENIC ACID—

Distribute 5-ml portions of the basal medium into each of three series of test-tubes, 18 to 20 mm in internal diameter and 15 to 16 cm in length. Add to one series of test-tubes 0-, 0·25-, 0·5-, 1·0-, 2·0-, 3·0- and 4·0-ml portions of dilute standard pantothenic acid solution, four tubes being used at each different volume. Dilute each solution to 10 ml with distilled water (standard series). Similarly prepare a sample series and an enzyme blank series, by using 0·5-, 1·0-, 2·0- and 4·0-ml portions of the sample extract and enzyme blank solution, respectively.

Cover each test-tube with an aluminium cap, sterilise at 115° C for 10 minutes, cool the contents of each tube, add one drop of the inoculum and incubate at 30° C for 72 hours.

Assess the growth response by titrating the contents of each tube to pH 6·8 with 0·1 N sodium hydroxide: use either a pH meter or bromothymol blue indicator solution for determining the end-point. Draw a curve of the responses to the doses of the standard, and read

off the potencies of the test extract by direct reading at not less than three concordant levels. Similarly read off the potency, if any, of the enzyme blank solution, and correct the figure obtained for the test extract accordingly. Multiply by the dilution factor, and calculate the potency of the test sample. Express the result as micrograms of pantothenic acid per gram of sample.

Appendix II

RECOMMENDED METHOD FOR EXTRACTING COMPOUND FEEDING STUFFS FOR THE DETERMINATION OF RIBOFLAVIN

For the microbiological determination of riboflavin by the assay procedure recommended in this Report, *i.e.*, that previously recommended by the Analytical Methods Committee[1] for assaying foods by using basal medium Y (see Note 1), the method described in this Appendix should be used for preparing and extracting the sample.

REAGENTS—

Light petroleum—Boiling-range 40° to 60° C.
Hydrochloric acid, 0·2 N.
Sodium acetate, 2·5 M.
Dilute sodium hydroxide solution—A 5 per cent. w/v solution in distilled water.

PROCEDURE

EXTRACTION—

Grind the sample to pass a 60-mesh sieve. Extract about 5 g of the ground sample, accurately weighed, with light petroleum in a Soxhlet apparatus until free fat and fatty acids are removed, and discard the extract. Remove the residual solvent from the extracted sample with a gentle current of warm air, mix the dry material with 50 ml of 0·2 N hydrochloric acid, and heat the mixture in saturated steam, in an autoclave, at 121° C for 15 minutes. Remove the digest to a dark room, and cool. Add 2 ml of 2·5 M sodium acetate, adjust the mixture to pH 4·6 with dilute sodium hydroxide solution, and dilute to 100 ml with distilled water. Filter at least half the mixture through a folded 15-cm Whatman No. 1 filter-paper, discard the first few millilitres of the filtrate, and adjust (see Note 2) a suitable portion of the filtrate to pH 6·8 with dilute sodium hydroxide solution, ignoring any precipitate that may form.

NOTES—

1. If desired, an electrometric method may be used for the titration.
2. If the sample under test has a high fat content, it is recommended that the filtrate be extracted with ether before the pH is adjusted.

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3. U.S. Department of Agriculture, "Agriculture Handbook No. 97," U.S. Government Printing Office, Washington, D.C.
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PART 5. REPORT OF THE VITAMINS (FAT-SOLUBLE) PANEL

The Determination of Fat-soluble Vitamins in Diet Supplements and Compound Feeding Stuffs

INTRODUCTION

THE Vitamins (Fat-soluble) Panel was set up under the Chairmanship of Mr. W. L. Sheppard. and its membership was: Mr. C. R. Louden, Mr. R. A. Rabnot, Mr. S. A. Reed, Mr. K. L. Smith, Mr. G. Walley, Dr. J. Williams and Mr. D. R. Wraige, with Dr. C. H. Tinker as Secretary, Subsequently, Mr. Rabnot, Mr. Smith and Mr. Wraige resigned, and Mr. L. Brealey and Mr. H. Pritchard joined the Panel. The Panel was appointed to ascertain whether or not methods could be recommended that would permit compound feeding stuffs to be assayed for β-carotene, vitamin A and vitamin D.

In preliminary discussions, the Panel agreed to seek methods:

(*i*) for determining the total amounts of the vitamins, *i.e.*, amounts naturally present in the ingredients of the unsupplemented ration together with amounts added as a supplement,

(*ii*) that are applicable to both high-potency diet supplements (pre-mixes) and supplemented feeding stuffs as fed to the animal, and

(*iii*) that can be carried out in laboratories without highly specialised and expensive apparatus.

Because of the nature of the materials used as supplements, the Panel thought it essential to make recommendations for the preparation of the bulk sample before samples for analysis are taken. These recommendations are given in Appendix I.

RESULTS AND RECOMMENDATIONS

VITAMIN A—

The method investigated most fully was one used extensively for feeding stuffs by one member of the Panel and involving saponification, column chromatography on alumina and a spectrophotometric finish. An alternative spectrophotometric finish,[1] involving dehydration of vitamin A with benzene and toluene-*p*-sulphonic acid, was also investigated, but as the method presented difficulties to some members of the Panel, it is recommended only as a short screening technique (see Appendix III).

The method given in the British Pharmacopoeia[2] was also examined, but it was rejected for the following reasons—

(*i*) With many samples, and particularly with diet supplements, the small irrelevant absorption is not linear. Its value can often be assessed by carrying out a blank determination on the unsupplemented basic feed. The B.P. procedure gives gross over-correction in these circumstances.

(*ii*) Distortion of the spectral curve of vitamin A occurs during the analytical procedure, particularly if the unsupplemented basic feed is mainly mineral in character. This distortion is enhanced if the extracted vitamin A is transferred from one solvent to another by a process involving evaporation, as in the B.P. method. The B.P. method itself, therefore, creates the need for a Morton and Stubbs type of correction when it is used for determining certain types of feeding stuffs.

The results of the first collaborative test by the selected method on a typical compound feeding stuff were promising, but it was clear that the analytical procedure required to be defined more closely, particularly for analysts unfamiliar with the technique. A second collaborative test, in which the recommended method as finally detailed in Appendices II(a), II(b) and II(c) were used, proved satisfactory. In this test, cod-liver oil of known potency was added to a vitamin-A-free meal, and the four collaborating laboratories reported results between 96 and 103 per cent. of the theoretical value. The Panel then investigated feeding stuffs containing more heavily protected vitamin concentrates, and also ones including milk powder and grass meal.

By this time the significance of the manner in which the additive is mixed with the basic feeding stuff had been realised. A single beadlet of concentrate may contain 1 to 10 i.u. of vitamin A, and the general level of additive distribution is usually one beadlet per gram of feeding stuff. The reagents used in the saponification stage are therefore required to react with about 25 beadlets, and for good replication it is essential to ensure that the beadlets are the same average size and are uniformly distributed. After great care had been taken in preparing the supplemented sample, satisfactory results were obtained even with the most highly protected compound feeding stuffs. In a collaborative test on a sample rich in grass meal, a result of 5·6 i.u. per gram was obtained by three members of the Panel, and 4·9 and 6·1 i.u. per gram by the other two. In a collaborative test on a feeding stuff containing milk powder, two members returned values of 12·8 i.u., one 13·5 i.u. and another member 15·0 i.u. per gram.

During the course of the collaborative tests, satisfactory recoveries were obtained when known amounts of vitamin A, either in cod-liver oil or in groundnut oil, were added to vitamin-A-free diets.

On the basis of these tests, the methods described in Appendices II(a), II(b) and II(c) are therefore recommended for the determination of vitamin A in diet supplements and compound feeding stuffs.

β-CAROTENE—

A method for determining β-carotene by an extension of the method for determining vitamin A, involving spectrophotometric measurement of the intensity of the colour of the carotenoid fraction eluted from the alumina column by the developing solvent containing 16 per cent. of ether, was investigated. A collaborative test, in which the method described in Appendix IV was used, on a typical compound feeding stuff by five members of the Panel gave results of $0·84 \pm 0·06$ mg of β-carotene per kilogram.

This method is therefore recommended for the determination of β-carotene in diet supplements and compound feeding stuffs.

VITAMIN D—

The Panel agreed that no reliable chemical method for determining vitamin D in compound feeding stuffs, at the level normally found, was available. More recent reports of success in this field by American workers were noted, and their publication was awaited with interest. A method for levels of about 100 i.u. per gram in materials having a low oil content was available.[3]

The biological test with rats will determine both vitamin D_2 and D_3 present in compound feeding stuffs. If vitamin D_3 only is to be determined, the biological test with chicks must be used. Attention is drawn to the fact that compound feeding stuffs contain substances that interfere with the availability of the vitamin to animals.

No recommendation is made for the determination of vitamin D in compound feeding stuffs.

SAMPLING—

The analyst can only be responsible for the result in relation to the sample sent to him. The Panel wishes to emphasise that the determination of vitamin A may be concerned with a supplemented feeding stuff that results from the addition of one variably potent beadlet of concentrate to each gram of feeding stuff. There is a danger that, if extreme precautions are taken in the preparation of the sample for the analyst, the sampler is doing the work of the compounder. This may be important in relation to the amount of additive needed by the chick in the early days of its life. It is clear that the preparation of the 2-lb sample sent for analysis is critical, and it is therefore strongly recommended that the procedure described in Appendix I for preparing the analytical sample be rigidly followed.

Appendix I

PREPARATION OF ANALYTICAL SAMPLE FOR FAT-SOLUBLE VITAMIN DETERMINATIONS

The analysis generally involves between 5 and 25 g of meal that may contain as little as one beadlet of protected vitamin per gram. The potency of each beadlet varies from 1 i.u. upwards. It is essential, therefore, that the bulk sample, of about 2 lb, be thoroughly homogenised before the analytical sample is weighed. This is best achieved by repeated grinding,

sieving and rolling on paper until at least 95 per cent. passes through a 25-mesh B.S. sieve. With high-potency diet supplements, loss of vitamin by adhesion to the walls of the grinder and sieve is avoided by initial dilution of the sample with ground maize to give a product containing about 50 i.u. per gram.

The sample should be analysed as soon as possible after grinding.

Appendix II(a)

RECOMMENDED METHOD FOR DETERMINING OF VITAMIN A IN DIET SUPPLEMENTS AND COMPOUND FEEDING STUFFS

PRINCIPLE OF METHOD—

The sample is saponified by heating it under reflux with ethanolic potassium hydroxide solution. The resulting vitamin A alcohol is extracted from the saponification mixture with light petroleum, isolated by chromatography on alumina and determined spectrophotometrically.

APPARATUS—

Apparatus for preparing alkaline alumina—(See Fig. 1.) This consists of a 100-ml round-bottomed flask with a ground-glass neck into which is fitted an adapter with a T-connection. Into the upper neck of the adapter is inserted an air-leak tube, the lower end of which is drawn out to a coarse capillary that extends to within about 0·5 cm of the bottom of the flask.

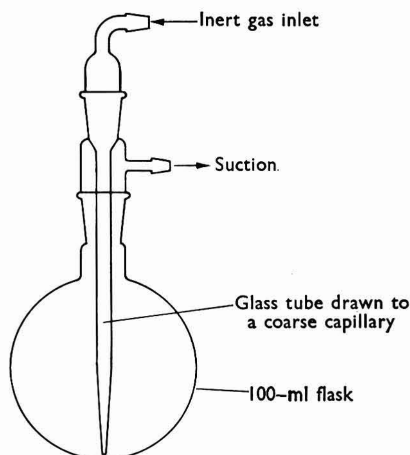


Fig. 1. Apparatus for preparing alkaline alumina

Chromatographic apparatus—(See Fig. 2.) This consists essentially of two chromatographic tubes. The upper chromatographic tube, whose construction and dimensions are shown in Fig. 2 (*a*), has a side-arm near its wider end, through which gas under pressure can be led. The upper end of the tube is closed with a bung, through which passes the stem of a 5-ml calibrated solvent reservoir. The stem, which carries a stop-cock, is bent at its lower end so that the opening just touches the inside of the tube. The lower chromatographic tube, whose construction and dimensions are shown in Fig. 2 (*b*), is fitted with a side-arm near its wider end, through which gas under pressure can be led, and a second side-arm carrying a stop cock. The wider end of the tube is closed with a bung, through which the narrower end of the upper chromatographic tube can pass.

When the two tubes are assembled into one unit, as shown in Fig. 2 (*c*), gas under pressure can be led to the upper portions of either tube through rubber tubing by manipulation of a three-way tap.

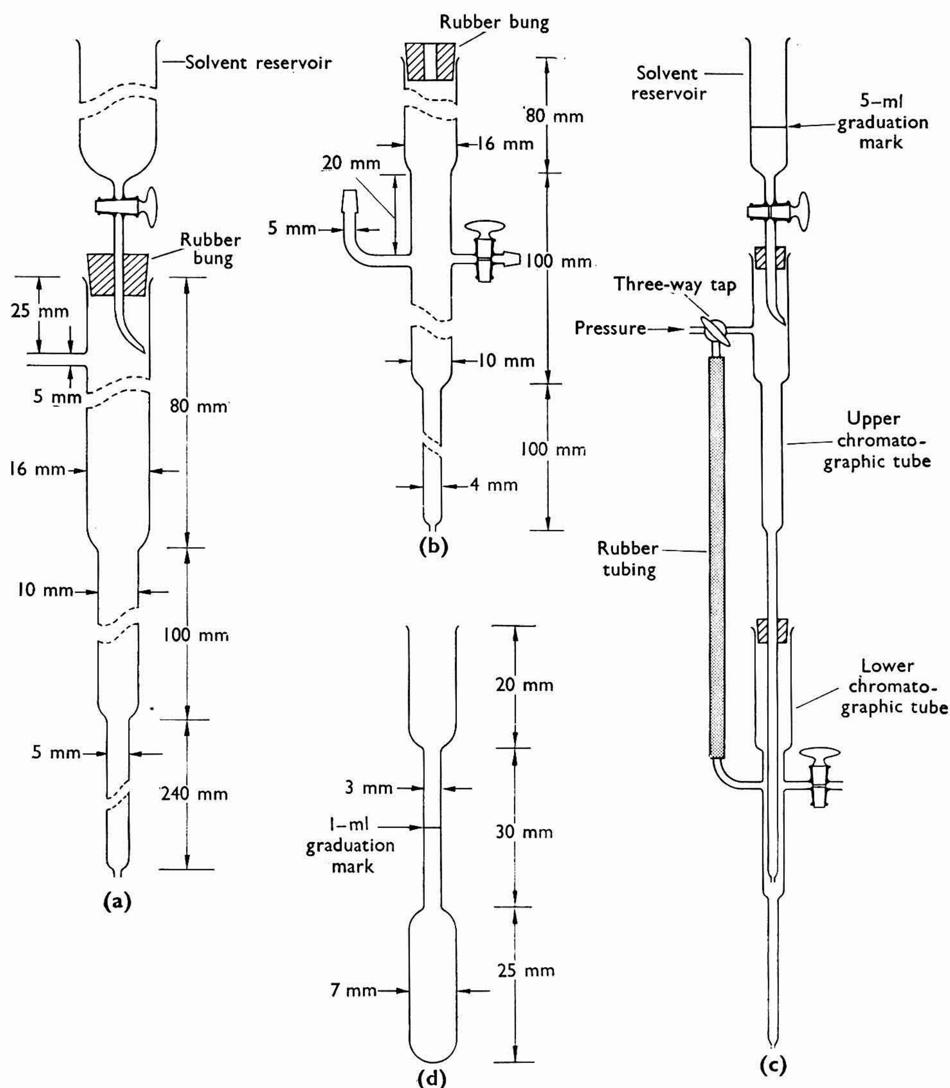


Fig. 2. Chromatographic apparatus

(*a*) Upper chromatographic tube
(*b*) Lower chromatographic tube
(*c*) Assembly
(*d*) Collection tube

Collection tubes—These receivers, whose construction and dimensions are shown in Fig. 2 (*d*), bear a graduation mark on the narrow portion indicating a capacity of 1 ml.

Pipette, 0·5 *ml*—With tip drawn out to a capillary.

Cuvettes—Two, preferably matched, each of quartz, and 1 cm in length.

REAGENTS—

Potassium hydroxide solution—Dissolve 160 g of potassium hydroxide in 100 ml of distilled water.

Absolute ethanol.

Light petroleum—Boiling-range 40° to 60° C.

Diethyl ether, peroxide-free.

Anhydrous sodium sulphate—Granular material dried in an oven at 105° C for 3 hours.

Developing solvents—Solutions in light petroleum containing 4, 8, 12, 16, 20, 24 and 36 per cent. v/v of ether. Both constituent solvents are dried over anhydrous sodium sulphate before mixing.

Quinol.

Sodium hydroxide solution—Dissolve 10 g of sodium hydroxide pellets in distilled water, and dilute to 100 ml with distilled water.

Phenolphthalein indicator solution—A 1·0 per cent. w/v solution in 95 per cent. v/v ethanol.

Inert gas—Hydrogen or oxygen-free nitrogen.

Alumina—Alumina trihydrate (a suitable quality can be obtained from the British Aluminium Co., Norfolk House, St. James's Square, London, S.W.1).

Alumina, type-1—Activate the fraction of alumina that passes through a 150-mesh B.S. sieve by heating at 800° C for 7 hours, and cool. Add 2 g of distilled water to each 98 g of activated alumina, mix well, and store in a stoppered bottle.

Alkaline alumina, type-2—Weigh 20 g of type-1 alumina into the flask, add 20 ml of sodium hydroxide solution, and assemble the apparatus as described above under "Apparatus." Connect the air-leak tube to a cylinder of inert gas and the T-connection of the adapter to a water pump, apply suction, pass a slow stream of inert gas through the mixture, and set aside for 1 hour. Immerse the flask in an oil-bath, raise the temperature slowly during 1 hour to 135° $\pm$ 2° C, and maintain the flask at this temperature for a further hour. Discontinue the gas stream, remove the flask from the oil-bath, allow to cool under vacuum, preferably overnight, and release the vacuum with inert gas.

Determine the moisture content of the product (loss on heating at 500° C for 2 hours), and adjust the moisture content to 12·5 $\pm$ 1 per cent. Transfer in approximately 1-g amounts (sufficient to prepare the lower chromatography tube—see below under "Chromatographic Separation of Vitamin A: Preparation of chromatographic tubes") to small glass tubes, and seal the tubes with wax.

The suitability of the prepared aluminas should be assessed by establishing in a preliminary test that vitamin A is eluted from the chromatography column by a developing solvent containing 24 per cent of ether.

Antimony trichloride reagent—To 800 ml of chloroform in a 1500-ml flask add 200 g of antimony trichloride, and heat under reflux until the solution is quite clear. Allow to cool, transfer to a 1-litre graduated measuring cylinder, add 30 ml of acetic anhydride, and dilute to 1 litre with chloroform. Store in an amber-coloured glass bottle.

The antimony trichloride should preferably be taken from a new bottle of the reagent; discoloured material must not be used.

PROCEDURE

The whole procedure must be carried out as quickly as possible and almost in the dark.

The effect of actinic light varies according to the material handled. Whenever possible it is advisable to use amber-coloured glassware; any filtration apparatus and other glassware should be masked by thick dark paper. These precautions are essential when solvents are removed, leaving the vitamin A spread as a thin film on the walls of the vessel.

SAPONIFICATION AND EXTRACTION OF SAMPLE—

Weigh 25 g of sample, prepared as described in Appendix I, into a 250-ml flat-bottomed flask, and add 60 ml of absolute ethanol, 0·2 g of quinol and 10 ml of potassium hydroxide solution. Boil under reflux on a water-bath for 30 minutes, with occasional swirling. Remove the flask from the water-bath, and cool.

Filter the contents of the flask through a 7-cm Whatman No. 54 filter-paper in a Buchner funnel into a 500-ml separating funnel, A, (see Fig. 3); at first, allow the liquid to filter without the aid of suction, and then gently apply suction until most of the solution has passed through the filter-paper. Wash the flask and residue with 50 ml of light petroleum, and pass the washings through the filter-paper into the separating funnel. Repeat the washing with three successive 35-ml portions of light petroleum, and then remove the Buchner funnel.

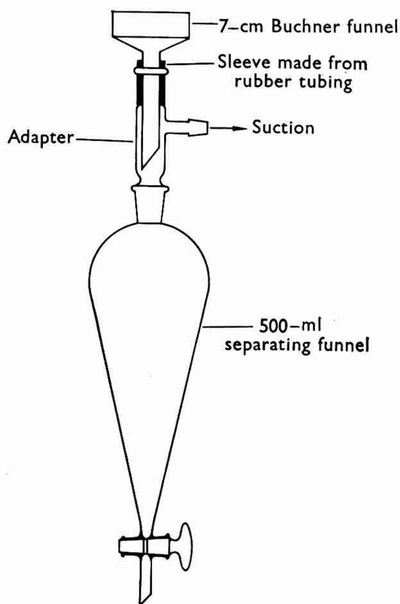


Fig. 3. Filtration assembly

To the combined filtrate and washings in the separating funnel, add 60 ml of distilled water, insert a stopper (preferably glass), shake vigorously, allow the layers to separate completely (this takes about 5 minutes), and run off the lower aqueous layer into a second 500-ml separating funnel, B. Swirl the light-petroleum layer in funnel A, set aside for about 30 seconds, and run off into funnel B any further portion of aqueous layer that separates. Introduce a few millilitres of distilled water, to act as a seal, into a third 500-ml separating funnel, C, and transfer to this funnel the light-petroleum layer in funnel A, through the neck of the latter; wash the neck of funnel A, inside and outside, with a few millilitres of light petroleum, and add the washings to the contents of funnel C. Wash funnel A thoroughly with three successive portions of light petroleum, transferring each washing in turn, through the neck of funnel A, to funnel B. Insert the stopper into the neck of funnel B, shake the funnel vigorously, allow the layers to separate for 5 minutes, and transfer the lower aqueous layer to funnel A and the upper light-petroleum layer to funnel C in the manner described above. Repeat the operations until four extractions of the aqueous liquid have been made and all the light-petroleum extracts are combined in funnel C. Discard the aqueous liquid.

Wash the combined light-petroleum extracts in funnel C by directing a jet of warm distilled water (35° to 40° C) from a wash-bottle (preferably of plastic) into funnel C, so that at first the water flows down the inside of the separating funnel and then through the light-petroleum solution. Swirl gently, allow the layers to separate, and run off the lower aqueous layer. Swirl the light-petroleum layer remaining in the separating funnel, set aside for about 30 seconds, and run off any further aqueous layer that separates. Repeat the washing twice

more with distilled water at 30° to 35° C, swirling more vigorously or even shaking gently. Test the last washing with phenolphthalein indicator solution, and, if free from alkalinity, proceed with the next stage; if the last washing is alkaline, continue the washing until the aqueous layer is free from alkalinity. If emulsions form at any stage, break them by adding 2 to 3 ml of absolute ethanol.

PRELIMINARY TREATMENT OF EXTRACT—

Dry the washed light-petroleum solution by adding anhydrous sodium sulphate and mixing, and transfer the dried solution to a two-necked 500-ml flask. Wash the sodium sulphate and the separating funnel with a little light petroleum, and add the washings to the solution in the flask. Evaporate the combined solution and washings to dryness on a water-bath in a current of inert gas. The last stages of the evaporation require the full attention of the analyst, because the residue in the flask must not be allowed to remain dry any longer than absolutely necessary. Immediately all the light petroleum has been removed, add 2 ml of absolute ethanol, and again evaporate to dryness in a current of inert gas; if the residue appears to be wet, repeat the addition of absolute ethanol and evaporation to dryness. Immediately dissolve the residue in 5 ml of light petroleum, and again evaporate to dryness in a current of inert gas. Repeat the dissolution in light petroleum and evaporation to dryness twice more. Finally, dissolve the residue in 3 to 5 ml of light petroleum and proceed to the next stage as soon as possible (see Note 1).

CHROMATOGRAPHIC SEPARATION OF VITAMIN A—

Preparation of chromatographic tubes—Place a pledget of cotton-wool in the lower tip of the upper chromatographic tube. Pour in light petroleum to a level half-way up the centre section, and add sufficient type-1 alumina to fill the lower section. Lead an inert gas under pressure to the top of the tube until the level of the light petroleum is about 1 mm above the top of the alumina column.

Similarly prepare the lower chromatographic tube, but with about 1 g of alkaline alumina in place of type-1 alumina.

Chromatography of solution—Transfer the light-petroleum solution from the preliminary treatment of extract to the top of the alumina column in the previously prepared upper chromatographic tube, and force the solution through the column by means of inert gas, led in under pressure through the side-arm fitted to the top of the tube. Develop the chromatogram, first with 5 ml of light petroleum and then with three successive 5-ml portions of developing solvent containing 4, 8 and 12 per cent. of ether, respectively; if β-carotene is to be determined by the method recommended in Appendix V, reserve the eluates, but if β-carotene is not to be determined, discard them.

Insert the lower end of the upper chromatographic tube through a rubber bung into the upper end of the previously prepared lower chromatographic tube, as shown in Fig. 2 (*c*), and continue the development of the chromatogram with four successive 5-ml portions of developing solvent containing 16, 20, 24 and 36 per cent. of ether, respectively, collecting the eluates in calibrated 1-ml collection tubes, until all the vitamin A is eluted (see Note 2). If β-carotene is to be determined, reserve the eluate obtained with the developing solvent containing 16 per cent. of ether. Mix the solution in each collecting tube by passing a few air bubbles from a drawn-out pipette through the liquid. Withdraw from each collection tube about 0·3 ml of solution, and test each portion separately for the presence of vitamin A with antimony trichloride reagent (see Note 3). From each tube that gives a positive (blue) reaction, transfer exactly 0·5 ml of solution to the same 10-ml calibrated flask, dilute the combined solution to the mark at 20° C with light petroleum, and determine the vitamin A in the solution by the method described below (see Note 4).

DETERMINATION OF VITAMIN A—

Thoroughly clean two 1-cm quartz cuvettes, fill each with light petroleum, and compare their optical densities with a spectrophotometer at several suitable wavelengths. If the optical densities at any particular wavelength differ by more than 0·001, clean the cuvettes again or make allowance for the difference.

Empty one cuvette, refill with the light-petroleum solution from the chromatographic separation of vitamin A, and cover the cuvettes with suitable lids. Measure the optical densities of the test solution against light petroleum with a spectrophotometer at 323, 324,

325, 326 and 327 mμ, and determine the wavelength of maximum absorption. Measure the optical densities of the test solution at wavelengths 15 mμ lower and 10 mμ higher than the wavelength of maximum absorption, and finally check the optical density at the wavelength of maximum absorption.

CALCULATIONS—

Calculate the vitamin-A content of the sample from the following expression:

$$\text{vitamin A (i.u. per g)} = \frac{\text{O.D.} \times 1830 \times 2 \times 10}{25 \times 100},$$

where O.D. = optical density of test solution at the wavelength of maximum absorption.

Calculate also the values of the ratios:

$$\frac{\text{O.D.}_{(peak - 15)}}{\text{O.D.}} \quad \text{and} \quad \frac{\text{O.D.}_{(peak + 10)}}{\text{O.D.}},$$

where O.D.$_{(peak - 15)}$ = optical density of test solution at a wavelength 15 mμ lower than the wavelength of maximum absorption, and

O.D.$_{(peak + 10)}$ = optical density of test solution at a wavelength 10 mμ higher than the wavelength of maximum absorption.

If either of these ratios exceeds 0·90, the determination is invalid, and must be repeated.

NOTES—

1. If necessary, the solution in light petroleum may be kept for 3 to 4 hours in a stoppered flask in a cool, dark place.

2. Ideally, elution of the vitamin A from the column should begin while the developing solvent containing 24 per cent. of ether is being passed through the column. In practice, satisfactory results are obtained even if the vitamin is not eluted until the developing solvent containing 36 per cent. of ether is used.

3. Usually, the vitamin A will be in the eluates collected in six to sixteen tubes, depending on the amount of vitamin put on the column and the volume of solvent in which it was dissolved.

4. If an ultraviolet spectrophotometer is not available, determine the vitamin A by the blue-value method, as described below—

Combine the 0·5-ml portions in the cell of a spectrophotometer, evaporate to dryness in a stream of inert gas, and immediately dissolve the residue in 1 ml of chloroform. Add 10 ml of antimony trichloride reagent so that mixing occurs, and measure the optical density at about 620 mμ; the colour develops rapidly and reaches a maximum intensity in about 3 to 5 seconds. Obtain the vitamin A concentration by reference to a previously prepared calibration graph relating units of activity to optical density.

Appendix II(b)

MODIFIED PROCEDURE FOR PRODUCTS IN WHICH THE PROTECTED VITAMIN IS DIFFICULT TO BREAK DOWN

APPARATUS—

The apparatus listed below, additional to that listed in Appendix II(a), is required—

Centrifuge—Sufficiently large to take at least two 250-ml cups.

Centrifuge tubes—Capacity about 250-ml.

REAGENTS—

The reagent specified below, additional to those listed in Appendix II(a), is required—

Diluted ethanol, 40 *per cent. v/v.*

PROCEDURE

SAPONIFICATION AND EXTRACTION OF SAMPLE—

Weigh 25 g of sample, prepared as described in Appendix I, into a centrifuge tube, add 60 ml of absolute ethanol, 0·2 g of quinol and 10 ml of potassium hydroxide solution, boil under reflux on a water-bath for 30 minutes, with occasional swirling, and remove the centrifuge tube from the water-bath. Plug the centrifuge tube (a cork wrapped in polythene film forms a convenient closure), spin in a centrifuge and decant the clear supernatant liquid into

a 500-ml separating funnel, A, containing 40 ml of distilled water. To the residue in the centrifuge tube add 50 ml of diluted ethanol, boil under reflux on a water-bath for 5 minutes, remove the centrifuge tube from the water-bath, plug the tube, spin it in a centrifuge, and again decant the clear supernatant liquid into funnel A. Repeat the extraction procedure with a further 50 ml of diluted ethanol, adding the clear supernatant liquid to funnel A.

To the residue in the centrifuge tube add 30 ml of distilled water, heat under reflux on a water-bath for 20 minutes, add 3 ml of potassium hydroxide solution, mix thoroughly, and add 50 ml of absolute ethanol. Boil under reflux on a water-bath for 5 minutes, and remove the centrifuge tube from the water-bath. Plug the centrifuge tube, spin in a centrifuge and decant the clear supernatant liquid into funnel A. To the residue in the centrifuge tube add 50 ml of light petroleum, extract the residue by shaking or stirring with a glass rod, allow to settle, and transfer the extract to funnel A. Extract the aqueous ethanolic layer as described in Appendix II(a) under "Saponification and Extraction of Sample" beginning at the words "insert a stopper (preferably glass), shake vigorously . . ." in the third paragraph, but use each fresh portion of light petroleum to extract the residue in the centrifuge tube before adding it to funnel A, and complete the determination as described in Appendix II(a).

Appendix II(c)

PROCEDURE FOR HIGH-POTENCY DIET SUPPLEMENTS

Weigh a suitably sized sample, prepared as described in Appendix I, saponify and extract with light petroleum as described in Appendix II(a) and dilute the final light-petroleum solution so that, from the expected potency, it contains approximately 8 i.u. per ml. Complete the determination as described in Appendix II(a).

At vitamin-A levels of 500 i.u. per g of diet supplement, it is desirable to obtain a result within 2 per cent. of the true figure. Every precaution, in the form of protection from light and speed of manipulation, must be taken against destruction of vitamin A and distortion of the spectral curve. Under good experimental conditions, the optical-density ratios often remain close to 0·86, even without the chromatographic purification of the light-petroleum extract on alumina. The chromatographic step may be omitted if the ratios do not exceed 0·90. The saponification stage should never be omitted, because it is unlikely that unprotected vitamin A will now be used in feeding stuffs.

Appendix III

RAPID SCREENING METHOD FOR DETERMINING VITAMIN A BY CONVERSION TO ANHYDRO-VITAMIN A

PRINCIPLE OF METHOD[1]—

Vitamin A in benzene solution is converted, at room temperature, to anhydro-vitamin A in the presence of toluene-*p*-sulphonic acid as catalyst. The increase in the optical density at 399 mμ resulting from the dehydration is proportional to the amount of vitamin A present, and can be used for the determination of this vitamin in unsaponifiable extracts.

APPLICABILITY—

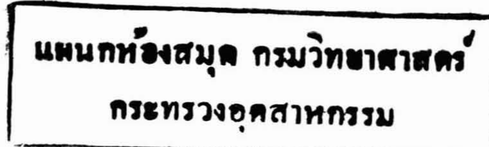
The method lacks the precision of the chromatographic method of Appendix II(a) and sometimes gives erratic results. It is not suitable for products containing grass meal.

APPARATUS—

Dry, in an oven, all glass apparatus used in the preparation of the catalyst solution and in the stages of the method described in this appendix, and allow to cool in a desiccator over anhydrous calcium chloride.

REAGENTS—

*Toluene-*p*-sulphonic acid*—Toluene-*p*-sulphonic acid monohydrate (obtainable from L. Light & Co., Colnbrook, Bucks.). Store in a desiccator over anhydrous calcium chloride or phosphorus pentoxide.



Benzene, dry—Shake 150 ml of analytical-reagent grade benzene with 5 mg of toluene-*p*-sulphonic acid, boil under reflux for 5 minutes, using a refluxing condenser fitted with a calcium chloride guard tube, loosely stopper the flask, and set aside overnight. Distil, and store the benzene over anhydrous calcium chloride. *Caution*—the vapour is toxic.

Absolute ethanol.

Light petroleum—Boiling-range 40° to 60°, free from aromatic hydrocarbons.

Quinol.

Potassium hydroxide solution—Dissolve 160 g of potassium hydroxide in 100 ml of distilled water.

Phenolphthalein indicator solution—A 1·0 per cent. w/v solution in 95 per cent. v/v ethanol.

Anhydrous sodium sulphate—Granular analytical-reagent grade material dried in an oven at 105° C for 3 hours.

Catalyst solution—Heat 15 mg of toluene-*p*-sulphonic acid under reflux on a sand-bath with 100 ml of dry benzene until dissolved, using a reflux condenser fitted with a calcium chloride guard tube. Distil off 10 ml of solvent to remove moisture, and allow the solution to cool, protecting it from moisture. Transfer to a 100-ml calibrated flask, and dilute to the mark with dry benzene. Freshly prepare the solution daily.

Procedure

Saponification and extraction of sample—

Saponify and extract a suitable weight of sample (see Note 1) as described in Appendix II(a).

Preliminary treatment of extract—

Dry the washed light-petroleum extract in separating funnel C, by adding anhydrous sodium sulphate and mixing, and decant the dried solution. Wash the sodium sulphate and the separating funnel with a few millilitres of light petroleum, and add the washings to the decanted solution. Adjust the volume of the combined solution and washings, either by evaporating in an atmosphere of inert gas, or by dilution with light petroleum to give a concentration of about 40 i.u. of vitamin A per ml, according to the expected potency.

Determination of vitamin A—

Transfer two 10-ml portions of the light-petroleum solution from preliminary treatment of extract to separate 25-ml thick-walled stoppered glass tubes, and evaporate to dryness under reduced pressure at 40° C. To one residue add 1 ml of dry benzene and 4 ml of catalyst solution (solution A), and to the other residue add 5 ml of dry benzene (solution B). Stopper each tube, shake the solutions, and set aside for 1 minute. To each solution add 1 g of anhydrous sodium carbonate, shake again, and set aside for not less than 1 minute. Remove the stoppers, spin each tube in a centrifuge until the supernatant liquids are clear, and decant the supernatant liquids into separate clean dry 1-cm cells. Measure the optical density of solution A against solution B with a spectrophotometer at 399 mμ. This value represents the increase in optical density resulting from dehydration of vitamin A.

Calculation—

Calculate the number of i.u. of vitamin A in the 10-ml portion of the light petroleum solution taken for the determination of vitamin A from the expression—

$$\text{vitamin A} = \frac{\text{O.D.}}{0{\cdot}0122}\ \text{i.u.},$$

where O.D. = optical density at 399 mμ; 0·0122 is the optical density corresponding to 1 i.u. of vitamin A in a 10-ml portion.

Hence calculate the vitamin A in the sample, and express the result as i.u. of vitamin A per g of sample.

Note

1. For compound feeding stuffs a sample weighing 5 to 10 g is suitable, and for diet supplements 0·25 g is sufficient.

Appendix IV

RECOMMENDED METHOD FOR DETERMINING β-CAROTENE IN DIET SUPPLEMENTS AND COMPOUND FEEDING STUFFS

The apparatus and most of the reagents described in Appendix II(a) are required for this method.

PROCEDURE

Combine the eluates obtained with developing solvents containing 4, 8 and 12 per cent. of ether and reserved in the chromatographic separation of vitamin A in the method described in Appendix II(a); include also the eluates obtained with the developing solvent containing 16 per cent. of ether, if these eluates do not contain vitamin A. If necessary, reduce the volume of the mixture by evaporation in an atmosphere of inert gas. Transfer the solution to a calibrated flask of suitable volume, and dilute to the mark with light petroleum.

With a spectrophotometer measure the optical density of the solution over the range 440 to 450 mμ in a 1-cm glass cuvette, against light petroleum. From the optical density at the wavelength of maximum absorption, calculate the extinction coefficient, ($E^{1\%}_{1cm}$), and multiply by 358 to obtain the equivalent β-carotene potency in i.u. per gram.

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The Sampling of Silicate Rock Powders for Chemical Analysis

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The errors introduced into the chemical analysis of silicate rocks when samples are taken from their heterogeneous powders are examined. These errors are dependent fundamentally on the weight multi-nomial distribution of the mineral particles, and, from this basis, exact expressions are derived for sampling errors of multi-mineral silicate rocks. Considerably simplified forms are shown for the special examples of bi-mineral rocks, uniform mineral densities and trace elements.

For uniform grain size, the variance is inversely proportional to the number of particles sampled, but for varying particle size, the total number of particles is of no special significance and is replaced by a weighted reciprocal mean.

Typical rock types are examined, and in general a 1-g sample of 72-mesh material is sufficient for the accurate determination of major elements. The use of smaller samples may introduce a significant error into a first-class analysis, and is not justified when there is ample material.

Trace elements, not associated with major elements, but forming characteristic minerals, are subject to a much greater relative sampling error than trace elements contained in major mineral species. As trace elements are frequently determined by spectrographic methods, in which small samples are used, sampling problems can arise, in spite of the greater permissible analytical latitude. Double sampling of the normal rock powder is a useful technique in these instances.

Abnormally high errors can be encountered when the trace element represents most or all of its characteristic mineral and this has a high grain density, as, for example, in the sampling of quartz for gold.

INSTRUMENTAL methods of analysis have recently undergone considerable development and have been used quite commonly in the analysis of silicate rocks. In spectrographic-arc methods, which are often used for determining trace elements, samples are restricted to a few milligrams. The determination of major elements by colorimetric and flame photometric methods requires solution concentrations of only a few micrograms of the elements per millilitre, and it would appear that samples of rock powder smaller than those used in classical analysis (about 1 g) could be taken with the advantages of increased ease of manipulation and less need for high dilutions. However, there is a risk that these smaller samples may not be representative of the average content of the powdered bulk specimen.

Silicate rocks, with few exceptions, contain two or more mineral species, and rock powders prepared from them will be heterogeneous. It is therefore possible that errors that could significantly affect the chemical determinations of constituent elements could arise from the use of small samples.

The calculations and discussions given below are an attempt to estimate these errors and to estimate the size of an adequate sample for determining an element in relation to the accuracy of the analytical method, the abundance of the element and the degree of fineness of the powdered rock sample. For this purpose it is necessary to calculate the sampling error, *i.e.*, the deviation of the distribution, of an element in samples drawn from the bulk specimens. As an element may be present in several mineral species, its variance will depend on the variances and co-variances of the distribution of these mineral species, which ultimately derive from the multi-nomial distribution. Initially it is assumed that all particles are of uniform volume, that each grain consists of only one mineral species

and that all mineral species are of fixed chemical composition. If the individual grains of the ground sample are smaller than the mineral crystals in the rock, it is almost certain that fracture will occur between the rock crystals of different mineralogical composition, and that each grain will consist almost entirely of one mineral species and not a mixture of mineral species. Rock samples for analysis usually pass a British Standard sieve of 72 meshes to the lineal inch, and this assumption will be valid for all but the ultra fine-grained rocks. For these, sampling errors will be less than calculated. The assumption, that the chemical composition of each mineral species is constant throughout the bulk specimen, is true if the whole of the rock specimen has originated from the same rock chipping, but may not be valid if the chippings come from a wide area. Here it is necessary to distinguish between the different forms of the same mineral.

The full mathematics are developed in the Mathematical Appendix and it is only necessary to quote here the final forms for the error.

When there are only two mineral species (1 and 2) in the rock, then, provided the standard error (s_E) is small, an appropriate assumption in the field of chemical analysis, an expression for this error can be derived—

$$s_E = (t_1 - t_2)\sqrt{\left(\frac{W_1 W_2}{n}\right)\left(\frac{d_1 d_2}{d^2}\right)} \quad \ldots \quad (4.3)$$

where W_1 and W_2 are the proportions of the mineral species 1 and 2, respectively, in the rock,

t_1 and t_2 are the fractions of the element E in these species,

d_1 and d_2 are the grain densities of the mineral species,

d is the specific gravity of the rock powder and

n is the number of mineral grains in the sample.

s_E will be in the same units as W_1 and W_2, and these may be expressed as percentages or parts per million, by weight.

If $t_2 = 0$ this equation can be simplified to—

$$\text{Fractional relative error, } S_E = \frac{s_E}{t_1 W_1} = \sqrt{\left(\frac{W_2}{W_1}\right)\left(\frac{d_1 d_2}{d^2}\right)\left(\frac{1}{n}\right)} \quad \ldots \quad (4.4)$$

Equation (4·3) may be rearranged into other forms that are more suitable for practical use—

$$s_E = (t_1 - t_2)\sqrt{\left(\frac{W_1 W_2}{Nw}\right)\left(\frac{d_1 d_2}{d^2}\right)} \quad \ldots \quad (4.5)$$

$$s_E = (t_1 - t_2)\sqrt{W_1 W_2\left(\frac{d_1 d_2}{d}\right)\left(\frac{v}{w}\right)} \quad \ldots \quad (4.6)$$

where N is the number of grains per unit weight of sample, so that $n = Nw$,

v is the volume of each particle and

w is the weight of sample taken.

These equations are similar to one derived by Baule and Benedetti-Pichler,[1] although in different forms.

When there are more than two mineral species the equations become considerably more complex. If there are m mineral species, and i and j represent any pair of these mineral species, then—

$$s_E^2 = \tfrac{1}{2}\sum_{i=1}^{m}\sum_{j=1}^{m}(\Delta t_i d_i - \Delta t_j d_j)^2\left(\frac{W_i W_j}{d_i d_j}\right)\left(\frac{1}{n}\right) \quad \ldots \quad (5.2)$$

where $\Delta t_i = t_i - t$,

W_i and W_j are the proportions of the mineral species i and j, respectively, in the rock,

d_i and d_j are the grain densities of these mineral species,

t_i and t_j are the fractions of E in i and j, respectively, and

t is the fraction of E in the rock.

This equation can be made simpler if all the densities of the mineral species are identical.

$$s_E^2 = \tfrac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} (t_i - t_j)^2 \left(\frac{W_i W_j}{n}\right) \qquad \ldots \quad \ldots \quad \ldots \quad (5.3)$$

To illustrate how this functions, this simplified form is written out in full for a rock containing three mineral species 1, 2 and 3—

$$s_E^2 = (t_1 - t_2)^2 \frac{W_1 W_2}{n} + (t_2 - t_3)^2 \frac{W_2 W_3}{n} + (t_3 - t_1)^2 \frac{W_3 W_1}{n} \qquad \ldots \quad \ldots \quad (5.4)$$

If the number of particles is large, the bi- or multi-nomial distribution approximates closely to the normal distribution, and the standard error (or deviation) represents a probability that 68 per cent. of the samples taken lie within such limits; twice the standard deviation ($2s_E$) represents a probability that 95 per cent. of the samples taken lie within such limits.

If the number of particles of a mineral is small, the distribution approaches the Poisson distribution, is highly skew and the normal approximation no longer holds. If the mineral densities differ greatly, these equations hold only if s_E is not too large (see the approximation made in deriving equation (2) in the Mathematical Appendix); in chemical analysis, however, this is a valid restriction. The equations are valid for all values of s_E if all the mineral densities are identical.

Sampling error for powders of non-uniform grain size

The discussion so far has been based on the simplifying assumption of uniform particle size, but, in practice, grinding and sieving operations will yield a powder whose grain size will vary considerably. It is therefore desirable to extend the theory to include this factor.

One complication is that a knowledge of the frequency distribution of particle size is required, and this distribution may depend on the nature of the material, the crushing and grinding equipment and the method of grinding and sieving. Rock powder for chemical analysis is ground to pass a sieve of specific mesh size. There is an upper limit to the grain size, but no lower limit. It is, therefore, easy to assign an upper limit to sampling error by taking the grain size as that of sieve, but to estimate the minimum sample required, knowledge of the distribution of different sized particles is necessary. It has been stated in this connection that this distribution is log-normal for many ground minerals.[2]

Equations for the standard error can be developed, on the assumption that the distribution of grain size is the same for each mineral species—an assumption that may not always be justified. The expression for standard deviation is generally similar to the one derived for the example of uniform grain size, except that the total number of particles in a sample has no significance, and must be replaced by a weighted reciprocal mean.

In the simple example, for two mineral species, we have—

$$s_E^2 = (t_1 - t_2)^2 \left(\frac{W_1 W_2}{\bar{N}\omega}\right) \left(\frac{d_1 d_2}{d^2}\right) \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7.2)$$

or

$$s_E^2 = (t_1 - t_2)^2 \left(W_1 W_2\right) \left(\frac{d_1 d_2}{d}\right) \left(\frac{\bar{v}}{w}\right) \qquad \ldots \quad \ldots \quad \ldots \quad (7.3)$$

where $\bar{N} = \sum_{h=1}^{k} \frac{g_h}{N_h}$ and $\bar{v} = \sum_{h=1}^{k} g_h v_h$

and where k is the number of groups of different particle size,

N_h is the number of particles per unit weight in the hth group,

v_h is the volume of these particles and

g_h is the fraction, by weight, of the hth group in the rock powder.

These equations are fully derived in the Mathematical Appendix.

It can be seen from these equations that the number of coarse particles will preferentially determine the standard deviation. The relationship between v_h and the sieve sizes of particles assumes that all particles are approximately spherical. This assumption may not always

be justified; for example, micas tend to flake on grinding. A full discussion on the "effective diameter" of sieved particles can be found in the literature.[3]

These equations permit examination of sampling errors for non-uniform particles, provided their grain-size distribution is known, so that values for $\bar{N}$ or $\bar{v}$ can be obtained. For the reasons given above, it is impossible to generalise except for the maximum sampling error. However, it is possible to estimate the minimum sampling levels by considering particular samples whose grain-size distribution has been determined.

Sampling error depends on several factors: rock type, weight of sample, sieve size and the size-frequency distribution of the powder between different grain sizes.

The optimum sieve size of rock powders for chemical analysis has been discussed by Hillebrand and Lundell,[4,5,6,7] who quote from investigations that have been carried out on the effect of grinding on composition. During grinding, water may be taken up or lost,[4] ferrous iron oxidised[5] and contamination introduced from the grinding equipment.[6] Hillebrand and Lundell[7] recommend the minimum grinding necessary for the decomposition of the sample, and they consider that a material passing a sieve of 30 meshes to the lineal centimetre (say, a B.S. sieve of 72 meshes per lineal inch) suitable for most rocks.

If the grains of the rock powder are of uniform size and just pass the sieve then each gram of material (sp.gr. 2·63) would contain $0{\cdot}77 \times 10^5$ particles. For equivalent sampling with smaller weights of material, approximately 100 mg of 150-mesh or 10 mg of 325-mesh material would have to be taken. Since powder passing a sieve will contain many particles smaller than the sieve size, the simple theory for uniform particle size, if the particle size is assumed to be that of the sieve, can be used to give a maximum value for the sampling error.

To calculate the minimum sample, the distribution of the differently sized particles must be known, and this may depend on the type of material ground and the equipment used.

Data supplied by Dr. P. G. Jeffery, who has carried out sieving tests on several rock specimens ground to pass a 72-mesh sieve, show that distribution depended to some extent on the material and method of grinding. There was little material of 72 to 85 mesh; about 40 to 60 per cent. was of 85 to 170 mesh; and between 12 and 30 per cent. passed a 350-mesh sieve. The total number of particles per gram of material exceeded 10^6. Estimates for $\bar{N}$ (the weighted reciprocal mean) were in the range 3×10^5 to 6×10^5.

Sampling errors for major rock elements

The sampling of silicate rocks can only be treated by examining suitably selected specific examples drawn from various rock types; a simple generalisation is not possible, since the error depends on factors other than sample size. The mode of occurrence of an element, which is in turn dependent on the rock type, will affect sampling. This is of particular importance for trace elements, which may occur either as a major essential constituent of a minor accessory mineral or as a trace constituent of a major mineral species. Trace elements constitute a separate problem in sampling and will be examined later.

To illustrate the sampling theory for major constituents, two hypothetical rocks of widely different type, one acidic and one basic, are considered.

Sample standard deviations for the constituent oxides of a hypothetical granite (see Table I) show that in this rock type, a sample of the order of $10^{5 \cdot 5}$ uniformly sized particles is more than adequate for a good analysis.

These errors are of the same order as those of a careful analysis of a feldspar quoted by Hillebrand and Lundell.[8] The use of smaller samples may introduce unnecessary error in a good analysis; in particular, both iron and silicon can be determined within closer limits than those when a sample of $10^{4 \cdot 5}$ uniformly sized particles is used. It has been shown above that 1 g of a normal heterogeneous rock powder passing a mesh of 72 meshes per lineal inch corresponds approximately to a sample size of 3×10^5 to 6×10^5 uniformly sized particles. Therefore, a 1-g sample of rock powder is adequate for a good analysis. It is undesirable to take smaller samples for the sake of manipulative convenience.

Although these calculations have been made for the specific example, the argument can be extended; albite could be replaced by plagioclase (calcium and aluminium replacing some sodium and silicon), or by alkali feldspar. Sampling errors would not be significantly different.

Sampling errors should be about the same for intermediate or basic rocks, except that lower sampling errors for the silicon dioxide constituent might be expected if there is no free quartz.

Calculations for a hypothetical basic rock (see Table II) show that, with the exception of silica, sampling errors are of the same order as those for a granite rock.

TABLE I

STANDARD DEVIATION OF SAMPLING FOR THE MINERALS AND MAJOR OXIDES OF AN IDEAL GRANITE

Composition of the granite, sp.gr. 2·63, was: quartz, sp.gr. 2·65, 35·0 per cent. an albite ($NaAlSi_3O_8$), sp.gr. 2·62, 60·0 per cent.; a biotite ($KFe_3(AlSi_3)O_{10}(OH)_2$), sp.gr. 3·1, 5·0 per cent.

Compound	Fraction of compound found in—			Amount found in rock, %	Standard deviation* for values of n of—	
	quartz	albite	biotite		$10^{5.5}$	$10^{4.5}$
Minerals—						
Quartz	1·0000	0·0000	0·0000	35·00	0·08	0·27
Albite ($NaAlSi_3O_8$)	0·0000	1·0000	0·0000	60·00	0·09	0·28
Biotite ($KFe_3(AlSi_3)O_{10}(OH)_2$)	0·0000	0·0000	1·0000	5·00	0·04	0·12
Oxides—						
Silica	1·0000	0·6873	0·3521	78·00	0·03	0·10
Alumina	0·0000	0·1944	0·0996	12·16	0·02	0·06
Iron oxide (FeO)	0·0000	0·0000	0·4270	$2·13_5$	0·02	0·06
Sodium oxide	0·0000	0·1183	0·0000	7·10	0·01	0·03

* Calculated by using equation (5.4).

TABLE II

STANDARD DEVIATION OF SAMPLING FOR THE MINERALS AND OXIDES OF AN IDEAL NORITE

Composition of the norite, sp.gr. 3·1, was: anorthite ($CaAl_2Si_2O_8$), sp.gr. 2·74, 50·0 per cent.; a hypersthene ($MgFeSi_2O_6$), sp.gr. 3·5, 50·0 per cent.

Compound	Fraction of compound found in—		Amount found in rock, %	Standard deviation* for values of n of—	
	hypersthene	anorthite		$10^{5.5}$	$10^{4.5}$
Minerals—					
Hypersthene ($MgFeSi_2O_6$)	1·0000	0·0000	50·00	0·09	0·28
Anorthite ($CaAl_2Si_2O_8$)	0·0000	1·0000	50·00	0·09	0·28
Oxides—					
Silica	0·5171	0·4319	47·45	0·01	0·02
Alumina	0·0000	0·3665	$18·32_5$	0·03	0·10
Iron oxide (FeO)	0·3093	0·0000	$15·46_5$	0·03	0·09
Magnesium oxide	0·1736	0·0000	8·68	0·02	0·05
Calcium oxide	0·0000	0·2016	10·08	0·02	0·06

* Calculated by using equation (4.3).

As there are many varities of igneous rocks it is unpractical to extend these calculations to cover all types. However, by confining attention to those simple instances when each constituent element is contained in only one mineral species present in a rock, a wide variety of rock types can be examined. The sample, for a particular element present to the extent of 5 per cent. of normal oxide, is calculated for a coefficient of variation of 0·50 per cent. Several elements present in characteristic and common rock-forming minerals are examined (see Table III). (Haematite, though not normally a rock-forming mineral, occurs in some altered olivine basalts and is included since it illustrates one aspect of sampling.) An inspection of Table III shows that the sample size varies considerably, but, with the exception of haematite, a sample size of 5×10^5 uniformly sized particles is adequate for rock types containing these minerals. This sample level is approximately equivalent to 1 g of rock powder passing a 72-mesh sieve. For a haematite-bearing rock, a significantly larger sample is required to give the same error, and this illustrates the point that, when a constituent forms a high percentage of a mineral species, sampling errors are more pronounced.

EFFECT OF MODE OF OCCURRENCE ON SAMPLING ERROR FOR MINOR CONSTITUENTS

Sampling errors for minor and trace elements will depend greatly on their mode of occurrence, *i.e.*, whether or not they are the essential element of a mineral. By applying the sampling theory to a minor or trace element present in only one mineral species, we have, from the Mathematical Appendix, the expression—

Coefficient of variation (percentage relative error), $S_E \times 100$

$$= \frac{s_E}{E} \times 100$$

$$= \sqrt{\left(\frac{W}{W_E}\right)\left(\frac{d_E}{d}\right)\left(\frac{1}{n}\right)} \times 100 \quad \ldots \quad (5.7)$$

where the subscript E is applied to the mineral species containing the element E, and W is the base of the units used for s_E, W_E and E, *i.e.*, 100 for percentages and 10^6 for p.p.m.

This equation shows that the relative standard deviation decreases as W_E increases. A trace or minor element, associated with a major mineral species by replacing a major element in the crystal lattice, will have a relative sampling error of the same order as the major element, and the same level of sampling will be suitable. If, however, the minor or trace element is present as a separate mineral species, in which it is an essential constituent, sampling errors will be much higher, and a higher level of sampling will be necessary. This is best illustrated by reference to the basic rock considered. If lithium is present as a trace constituent (say 400 p.p.m. as lithium oxide) it could either replace magnesium or iron present in the hypersthene (case A), or be concentrated as a discrete mineral, spodumene, $LiAlSi_2O_6$ (case B). These calculations, summarised in Table IV, show how the error varies with sample size and distribution, and that it is considerably greater in case B than in case A.

TABLE III

SAMPLING FOR SOME MAJOR ELEMENTS PRESENT IN TYPICAL ROCK-FORMING MINERALS

Elements present at 5·00 per cent. as oxides; coefficient of variation = 0·50 per cent.

Mineral	Constituent oxide	Sample size n* ($\times 10^5$)
Pyroxene—		
Enstatite ($Mg_2Si_2O_6$)	MgO	2·81
Ferrosilite ($Fe_2Si_2O_6$)	FeO	3·96
Olivine—		
Forsterite (Mg_2SiO_4)	MgO	4·19
Fayalite (Fe_2SiO_4)	FeO	5·23
Feldspar—		
Orthoclase ($KAlSi_3O_8$)	K_2O	0·96
Albite ($NaAlSi_3O_8$)	Na_2O	0·55
Anorthite ($CaAl_2Si_2O_8$)	CaO	1·22
Mica—		
Phlogopite ($KMg_3(AlSi_3)O_{10}(OH)_2$)	MgO	1·92
Biotite ($KFe_3(AlSi_3)O_{10}(OH)_2$)	FeO	2·97
Muscovite ($KAl_2(AlSi_3)O_{10}(OH)_2$)	Al_2O_3	2·68
Haematite (Fe_2O_3)	Fe_2O_3	15·2

* Calculated by using equation (4.4). Value for $\frac{d_1 d_2}{d^2}$ taken as 1·00, except for haematite where it was taken as 2·00.)

Certain minor and trace elements are present in silicate rocks as essential constituents of minor accessory minerals disseminated throughout the rock type—for example, zirconium in zircon, titanium in ilmenite, sulphur in pyrites and carbonate in calcite. From the previous discussion, it is clear that such elements, being major constituents of minerals, are subject to greater sampling errors than trace elements that replace a major element in a mineral—for example, rubidium or caesium (associated with potassium) and strontium (associated with calcium).

Table V shows the sample size for elements contained in minor accessory minerals for chosen coefficients of variation and present at a level at which they are often found in rocks. Of the minor constituents both sulphur (as FeS_2) and phosphorus (as P_2O_5) require a 1-g

sample of 72-mesh powder for a coefficient of variation of 2 per cent., which is adequate for a minor constituent; a semi-micro sample of 100 mg would be insufficient. For trace elements normally determined by spectrographic-arc methods, a coefficient of variation of 10 per cent. has been allowed because of the low analytical accuracy of such methods. Even for this coefficient of variation, it can be seen that, for trace elements present as major constituents of trace minerals, samples of between 4×10^5 and 8×10^5 uniformly sized particles are required. Since 10-mg samples are usual in spectrographic analysis it is clear that an extremely fine rock powder is needed, and if we assume that the distribution of fine rock powder between different particle sizes is the same as that for 72-mesh powder, then a 325-mesh powder will be required. Since the normal rock powder for rock analysis will be 72-mesh, it is desirable to take the final spectrographic sample from a 1-g sample of the bulk powder that has been finely ground to pass a 325-mesh sieve. This technique of double-sampling will keep errors to a minimum.

TABLE IV

EFFECT OF MODE OF OCCURRENCE ON SAMPLE ERROR

Value of $n = 10^5$

Mode of occurrence	Amount of mineral in the rock, %	Standard deviation,* p.p.m.	Fraction of lithium oxide in mineral	Amount of lithium oxide in the rock, p.p.m.	Standard deviation,* p.p.m.
Case A—					
Trace element in pyroxene ($MgFeSi_2O_6$), sp.gr. 2·62	50·00	1580	0·00080	400	1·3
Case B—					
Element in spodumene ($LiAlSi_2O_6$), sp.gr. 3·2	0·50	250	0·0800	400	20

* Calculated by using equation (5.7).

TABLE V

SAMPLING FOR SOME MINOR AND TRACE ELEMENTS PRESENT AS CHARACTERISTIC CONSTITUENTS OF ACCESSORY MINERALS

The elements are present at levels normally to be expected in silicate rocks, with the exception of ferrous sulphide, carbon dioxide and gold.

Mineral	Constituent mineral*	Amount of constituent present, p.p.m.	$\frac{d_1 d_2}{d^2}$	Coefficient of variation, %†	Sample size n
Pyrite (FeS_2)	FeS_2	10,000	2·0	2·0	$5·0 \times 10^5$
Ilmenite ($FeTiO_3$)	TiO_2	10,000	1·75	2·0	$2·3 \times 10^5$
Calcite ($CaCO_3$)	CO_2	10,000	1·0	2·0	$1·0 \times 10^5$
Apatite ($Ca_5(PO_4)_3F$)	P_2O_5	2000	1·2	5·0	$1·0 \times 10^5$
Chromite ($FeCr_2O_4$)	Cr	200	1·75	10·0	$4·0 \times 10^5$
Chalcopyrite ($CuFeS_2$)	Cu	100	1·6	10·0	$5·1 \times 10^5$
Zircon ($ZrSiO_4$)	Zr	100	1·75	10·0	$8·7 \times 10^5$
Gold (Au)	Au	5	7·2	10·0	$1·4 \times 10^8$

* As normally reported in an analysis.
† Calculated by using equation (5.7).

Although gold is not a common trace constituent of silicate rocks, the example of gold in quartz has been examined as sampling errors are unusually high. For quartz containing 2 p.p.m. of gold, and if a coefficient of variation of 10 per cent. in the sampling is assumed, a sample of between 40 and 50 g of 72-mesh powder would be required.

CONCLUSION

A rock sample of 1 g of 72-mesh powder, the optimum size for analysis, is adequate for the accurate determination of the major elements in most rock types. The use of smaller samples is not desirable, because they are not adequate for all rock types. Certain trace elements, such as those present in characteristic minerals, can present sampling problems in spectrographic analysis when small samples are taken. An important factor is the fraction of an element in a mineral species; when this and the specific gravity of the mineral species is high, larger samples are required to offset greater sampling errors.

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Mathematical Appendix

The object of this mathematical treatment is to derive expressions for the variance of the distribution, var(E), of an element E in samples of rock powder drawn from the bulk specimen. Since the element may be present in several mineral species, its variance will depend on the variances and co-variances of these mineral species. The distribution of an element in a rock powder has certain unusual statistical features. Generally, bi- and multi-nomial statistics have been concerned with the distribution of particles on a simple numerical basis, but here a weight distribution is important, and relatively little attention has been paid to these statistics.[9] Statistical theory is often applied to the simple problem where an item either possesses or does not possess an attribute. The situation under consideration is more complex, and a mineral particle may possess an attribute (an element) in varying amounts.

To avoid confusion in this appendix, the terms weight variance and weight co-variance will be used when considering distribution by weight, and particle variance and particle co-variance when considering distributions of the usual numerical type. The bulk of the mathematical problem lies in the derivation of the connection between the weight co-variances and the particle co-variances of the mineral species. Although the former is required for the calculation of the element variance, the basic statistical model for sampling (the multi-nomial distribution) produces the latter.

There are three steps in the mathematical derivation.

1. Finding an expression for var(E) in terms of the mineral weight co-variances, cov $(i,j)_w$.
2. Finding the relationship between the mineral weight co-variances, cov $(i,j)_w$, and the mineral particle co-variances, cov $(i,j)_n$.
3. Applying the multi-nomial distribution that derives cov $(i,j)_n$, and hence cov $(i,j)_w$, and subsequently var(E).

In the simplified treatment it is assumed that all the particles in a sample are of uniform volume and that each particle consists of one mineral species only; this is true if the mineral crystal size is greater than the grain size. A further assumption is that the chemical composition of each mineral species is constant throughout the bulk specimen; this will be true if all the rock specimen has originated from the same parent field chipping.

THE RELATIONSHIP BETWEEN var(E) AND cov $(i,j)_w$

For a single sample, weight w, drawn from the bulk rock powder containing m mineral species we have—

$$\delta w_E = \sum_{i=1}^{m} t_i \delta w_i = \sum_{i=1}^{m} x_i, \text{ say,}$$

where δw_E and δw_i are the deviations from the true content of the element E and the ith mineral species in the rock, respectively, expressed in terms of weight, and

t_i and t_j are the fractions of E in the mineral species i and j, respectively.

Squaring, we have—

$$\delta w_E^2 = \left(\sum_{i=1}^{m} x_i \right)^2$$

Expanding the right-hand side—

$$\left(\sum_{i=1}^{m} x_i\right)^2 = x_1^2 + x_2^2 + x_3^2 + \ldots + x_m{}^2$$
$$+ x_1 (x_2 + x_3 + x_4 + \ldots + x_m)$$
$$+ x_2 (x_1 + x_3 + x_4 + \ldots + x_m)$$
$$+ x_3 (x_1 + x_2 + x_4 + \ldots + x_m)$$
$$+ \ldots .$$
$$+ x_m (x_1 + x_2 + x_3 + \ldots + x_{m-1})$$

Collecting these terms together and giving the terms within the brackets the general subscript j, provided that j cannot equal the particular value of i in the second or subsequent terms the right-hand side becomes—

$$\sum_{i=1}^{m} x_i^2 + x_1 \Sigma x_j + x_2 \Sigma x_j + x_3 \Sigma x_j + \ldots + x_m \Sigma x_j$$

Substituting for x_i and x_j, and summing, we have—

$$\delta w_{\mathrm{E}}^2 = \sum_{i=1}^{m} t_i^2 \delta w_i^2 + \sum_{i=1}^{m} \sum_{j=1}^{m} t_i t_j \delta w_i \delta w_j \quad (i \neq j) \quad \ldots \quad (1.1)$$

Expanding for all samples we have—

$$\mathrm{var(E)} = \sum_{i=1}^{m} t_i^2 \, \mathrm{var}(i)_w + \sum_{i=1}^{m} \sum_{j=1}^{m} t_i t_j \, \mathrm{cov}(i,j)_w \quad (i \neq j) \quad \ldots \quad (1.2)$$

where var(E) is the weight variance of E,
$\mathrm{var}(i)_w$ is the weight variance of i and
$\mathrm{cov}(i,j)_w$ is the weight co-variance for any pair of mineral species i and j.

Since w is constant, $\sum_{i=1}^{m} \delta w_i = 0$, and $\delta w_i \sum_{i=1}^{m} \delta w_i = 0$ it follows that—

$$\delta w_i^2 + \delta w_i \sum_{j=1}^{m} \delta w_j = 0 \quad (i \neq j) \qquad \text{for a single sample.}$$

Therefore, for all samples for the species i—

$$\mathrm{var}(i)_w + \sum_{j=1}^{m} \mathrm{cov}(i,j)_w = 0 \quad (i \neq j)$$

Substituting in equation (1.2), we have—

$$\mathrm{var(E)} = -\tfrac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} (t_i - t_j)^2 \mathrm{cov}(i,j)_w \quad \ldots \quad (1.3)$$

This gives the variance of an element in terms of co-variances of pairs of minerals. or two mineral species, 1 and 2, this reduces to—

$$\mathrm{var(E)} = -(t_1 - t_2)^2 \, \mathrm{cov}\,(1,2)_w \quad \ldots \quad (1.4)$$

THE RELATIONSHIP BETWEEN COV $(i,j)_w$ AND COV $(i,j)_n$

It is now required to find the relationship between the weight co-variances, cov $(i,j)_w$, and the particles co-variances, cov $(i,j)_n$, of the mineral species i and j.

If a sample of n particles is taken, and the deviation of the number of particles for a species i from the mean of all samples n_i is δn_i, then there will be a change of weight of i, δw_{iA}, associated with this change. This change of weight is given by—

$$\delta w_{iA} = vd_i\delta n_i$$

where v is the volume of each particle, and d_i is the grain density of the ith mineral species.

If, however, the density of each mineral species is different, then the mean density of the sample will vary with δn_i, and the weight of sample to correspond with n particles will no longer be the mean of all samples, w, but $w + \delta w$, and a further sample of $-\delta w$ will have to be taken. The change in weight of i due to this factor is given by—

$$\delta w_{iB} = -\frac{w_i}{w}\delta w$$

where w_i is the mean weight of i in all samples. Let—

$$\delta w_{iAB} = \delta w_{iA} + \delta w_{iB} = vd_i\delta n_i - \frac{w_i}{w}\delta w$$

Now the sample $-\delta w$ will be subject to the same distribution as the initial sample, and there will be a similar proportional deviation, $\delta' w_{iAB}$, where—

$$\delta' w_{iAB} = -\frac{\delta w}{w}\delta w_{iAB}$$

This argument can be repeated indefinitely for the second and subsequent orders, so that—

$$\delta'' w_{iAB} = -\frac{\delta w}{w}\delta' w_{iAB} = \left(\frac{\delta w}{w}\right)^2 \delta w_{iAB} \qquad \text{for the second order.}$$

The total deviation in weight of the species i, δw_i, is now given by—

$$\delta w_i = \delta w_{iAB}\left(1 - \frac{\delta w}{w} + \left(\frac{\delta w}{w}\right)^2 - \left(\frac{\delta w}{w}\right)^3 + \ldots\right)$$

If δw is small, then $\delta w_i \approx \delta w_{iAB}$, and—

$$\delta w_i = vd_i\delta n_i - \frac{w_i}{w}\delta w \qquad \text{as a first order approximation.}$$

If there are m minerals—

$$w\delta w_i = v\left(wd_i\delta n_i - w_i\sum_{i=1}^{m} d_i\delta n_i\right) \quad .. \quad .. \quad .. \quad .. \quad (2)$$

As the mathematical treatment for two-mineral species is somewhat different from that for three- (or more) mineral species, it will be considered separately.

TWO-MINERAL SPECIES—

The subscripts 1 and 2 are applied, when appropriate, to the symbols already defined.

For the mineral species 1 and 2, equation (2) becomes—

$$w\delta w_1 = v\,(w_2d_1\delta n_1 - w_1d_2\delta n_2) \text{ and } w\delta w_2 = v(w_1d_2\delta n_2 - w_2d_1\delta n_1)$$

Combining the equations, we have—

$$w(t_1\delta w_1 + t_2\delta w_2) = v(t_1 - t_2)(w_2d_1\delta n_1 - w_1d_2\delta n_2)$$

where t_1 and t_2 are the fractions of element E in 1 and 2, respectively.

Squaring, we have—

$$w^2(t_1 - t_2)^2\delta w_1\delta w_2 = v^2(t_1 - t_2)^2(w_2d_1 + w_1d_2)^2\delta n_1\delta n_2$$

Because $\quad \delta w_1{}^2 = \delta w_2{}^2 = -\delta w_1\delta w_2$ and

$$\delta n_1{}^2 = \delta n_2{}^2 = -\delta n_1\delta n_2$$

and since $\quad w = vnd,\ w_1 = vn_1d_1$ and $w_2 = vn_2d_2$,

the last equation can be re-written—

$$(t_1 - t_2)^2 \delta w_1 \delta w_2 = v^2 (t_1 - t_2)^2 \frac{d_1^2 d_2^2}{d^2} \delta n_1 \delta n_2$$

Since this is for one sample, the equation for all samples becomes—

$$(t_1 - t_2)^2 \operatorname{cov}(1,2)_w = v^2 (t_1 - t_2)^2 \left(\frac{d_1^2 d_2^2}{d^2} \right) \operatorname{cov}(1,2)_n \qquad (3.1)$$

The left-hand side of this equation is var(E), see equation (1.4).

The bi-nomial distribution[10] produces the equation—

$$\operatorname{cov}(1,2)_n = -\frac{n_1 n_2}{n}$$

Substituting this expression and equation (1.4) in equation (3.1), we have—

$$\operatorname{var(E)} = (t_1 - t_2)^2 \left(\frac{d_1 d_2}{d^2} \right) \frac{w_1 w_2}{n} \qquad (4.1)$$

If W_1 and W_2 are the proportions, by weight, of 1 and 2, respectively in the rock, and the sampling error for the element (the standard deviation of the distribution s_E) is in the same units, then—

$$s_E^2 = (t_1 - t_2)^2 \left(\frac{d_1 d_2}{d^2} \right) \frac{W_1 W_2}{n} \qquad (4.2)$$

The other forms of this equation have already been given, as equations (4.3) to (4.6).

m MINERAL SPECIES—

The subscripts i and j apply for any pair of mineral species, and are applied, when appropriate, to symbols already defined.

From equation (2), for the species i we have—

$$w t_i \delta w_i = v \left(w d_i t_i \delta n_i - w_i t_i \sum_{i=1}^{m} d_i \delta n_i \right)$$

For all species, this becomes—

$$w \sum_{i=1}^{m} t_i \delta w_i = v \left(\sum_{i=1}^{m} w d_i t_i \delta n_i - \sum_{i=1}^{m} w_i t_i \sum_{i=1}^{m} d_i \delta n_i \right)$$

where t_i is the fraction of element E in i.

If t is the fraction of E in the whole of the rock powder, the above equation can be written—

$$\sum_{i=1}^{m} t_i \delta w_i = v \sum_{i=1}^{m} (t_i - t) d_i \delta n_i$$

Substituting Δt_i for $(t_i - t)$, and squaring both sides, we have—

$$\sum_{i=1}^{m} t_i^2 \delta w_i^2 + \sum_{i=1}^{m} \sum_{j=1}^{m} t_i t_j \delta w_i \delta w_j = v^2 \left(\sum_{i=1}^{m} \Delta t_i^2 d_i^2 \delta n_i + \sum_{i=1}^{m} \sum_{j=1}^{m} \Delta t_i \Delta t_j d_i d_j \delta n_i \delta n_j \right) \qquad (i \neq j)$$

It has already been proved that—

$$\delta w_i^2 + \sum_{j=1}^{m} \delta w_i \delta w_j = 0 \qquad (i \neq j)$$

and by similar reasoning it can be shown that—

$$\delta n_i^2 + \sum_{j=1}^{m} \delta n_i \delta n_j = 0 \qquad (i \neq j)$$

Substituting for δw_i^2 and δn_i^2, and applying this argument for one sample to all samples, we have—

$$\sum_{i=1}^{m} \sum_{j=1}^{m} (t_i - t_j)^2 \mathrm{cov}(i,j)_w = v^2 \sum_{i=1}^{m} \sum_{j=1}^{m} (\Delta t_i d_i - \Delta t_j d_j)^2 \mathrm{cov}(i,j)_n \quad \ldots \quad (3.2)$$

The left-hand side is twice var(E). Applying the multi-nomial distribution for any pair i and j,[10] $\left(\mathrm{cov}(i,j)_n = -\frac{n_i n_j}{n}\right)$, we have—

$$\mathrm{var(E)} = \tfrac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} (\Delta t_i d_i - \Delta t_j d_j)^2 \frac{w_i w_j}{d_i d_j} \left(\frac{1}{n}\right) \quad \ldots \quad \ldots \quad \ldots \quad (5.1)$$

This is the general expression for the sampling error for elements in a multi-mineral silicate rock. Other forms of this equation have already been given, as equations (5.2), (5.3) and (5.4).

MINOR AND TRACE ELEMENTS—

For a minor or trace element present in a single characteristic mineral, the following approximations can be applied—

$$t \approx 0, \text{ and } \sum_{j=1}^{m} \frac{w_j}{d_j} \approx \frac{w}{d} \qquad (j \neq \mathrm{E})$$

Assigning symbols with a subscript E to the trace element, equation (5.1) reduces to—

$$\mathrm{var(E)} = t_{\mathrm{E}}^2 \left(\frac{d_{\mathrm{E}}}{d}\right) \left(\frac{w_{\mathrm{E}} w}{n}\right) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5.5)$$

If the relative amount of the element in the rock is E, the relative amount of the characteristic mineral is W_{E}, and W expresses the units used, *i.e.*, 100 for percentages and 10^6 for p.p.m., then, if s_{E} is in the same units—

$$S_{\mathrm{E}}^2 = \frac{s_{\mathrm{E}}^2}{\mathrm{E}^2} = \left(\frac{W}{W_{\mathrm{E}}}\right) \left(\frac{d_{\mathrm{E}}}{d}\right) \left(\frac{1}{n}\right) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5.6)$$

where S_{E} is the fractional relative error.

NON-UNIFORM PARTICLE SIZE—

The equations derived so far have been based on the simplifying assumption that all particles are of equal volume. In practice, particle size will vary considerably in a ground and sieved rock powder, and it is desirable to extend the theory to cover the general case.

For this purpose, the rock powder is considered as being divided into a number of classes, where each class contains all the particles of one size. It is assumed that the mineralogical composition of each class is identical.

The variance of the element, E, will only equal the sum of its variances in each class; the variance between each class has no effect on var(E).

For the hth class

$$\mathrm{var(E)}_h = \tfrac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} (\Delta t_i d_i - \Delta t_j d_j)^2 \left(\frac{w_{ih} w_{jh}}{d_i d_j}\right) \left(\frac{1}{n_h}\right) \quad \ldots \quad \ldots \quad (6)$$

where the subscript h denotes the symbols for the hth species.

Consider the factor $\frac{w_{ih}w_{jh}}{n_h}$. The sum of all these factors for k such groups is—

$$\sum_{h=1}^{k} \frac{w_{ih}w_{jh}}{n_h}$$

If g_h is the fraction of h present by weight, $w_h = g_h w$, we have—

$$\sum_{h=1}^{k} \frac{g_h^2}{n_h} w_i w_j, \text{ which can be reduced to } \frac{w_i w_j}{\bar{n}},$$

where $\bar{n}$ is the weighted reciprocal mean given by $\frac{1}{\bar{n}} = \sum_{h=1}^{k} \frac{g_h^2}{n_h}$

Summing the variances of E in all the classes, as given by equation (6), we have

$$\text{var(E)} = \tfrac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} (\Delta t_i d_i - \Delta t_j d_j)^2 \left(\frac{w_i w_j}{d_i d_j}\right) \left(\frac{1}{\bar{n}}\right) \quad \ldots \quad \ldots \quad \ldots \quad (7.1)$$

This is similar in form to the equation (5.1), derived for uniform particle size, with n replaced by the weighted reciprocal mean $\bar{n}$. Other forms of this equation have already been quoted, as equations (7.2) and (7.3), for the simple example of two mineral species.

The question of the distribution of the differently sized particles has already been examined from a practical aspect. It has been stated, in general terms, that the log-normal law often applies to the distribution of particle size, if the powder has been obtained by milling, crushing and grinding from quartz, granite, calcite, limestone or alumina.[2]

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A Thermogravimetric Study of the Selenites of Hafnium and Zirconium

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A study of the thermal decomposition of zirconium selenite and hafnium selenite was made, with the use of a Stanton recording thermobalance, to assess the usefulness of these compounds for determining the two metals in admixture. The results show that the use of these compounds is to be recommended, provided that care is taken to ensure the complete conversion of the basic selenite to the normal selenite.

SELENOUS acid, as a reagent for zirconium, was first introduced in 1920 by Smith and James,[1] and its application was investigated more thoroughly by Simpson and Schumb.[2] The procedure used was precipitation of the gelatinous basic selenite from acid solution and subsequent ignition to the oxide. Simpson and Schumb discovered that this basic selenite was converted to the crystalline normal selenite by prolonged digestion just below the boiling-point in the presence of excess of reagent.

Subsequently, Claasen[3] described the development of methods for determining zirconium and hafnium in admixture. He showed that the selenite was the only stoicheiometric compound of zirconium that could be weighed directly and then ignited to the oxide; hafnium was shown to behave similarly. Claasen's procedure involved precipitating the metals as their normal selenites and weighing the dried precipitate. This was either ignited to the oxide and weighed again, or dissolved and the liberated selenous acid determined iodimetrically.

The gravimetric procedure was used satisfactorily by Schumb and Pitman[4] for following the course of a separation of the two elements.

The thermogravimetric examination of these compounds has been reported in two papers. The first, by Stachtchenko and Duval,[5] includes an examination of the basic selenite of zirconium. This was claimed to be a mixture of the basic and normal selenites and had a calculated molecular weight of 330 compared with 345·14 for $Zr(SeO_3)_2$. The thermogram showed constant weight between 100° and 220° C, when decomposition began. The oxide level was obtained "towards 900° C."

The second paper, by Dautel and Duval,[6] describes the thermolysis of hafnium compounds, including both the basic selenite and the normal selenite. The basic selenite was shown to be of indefinite composition, whereas the normal selenite, prepared by Claasen's method, was crystalline, and the calculated molecular weight agreed with the composition $Hf(SeO_3)_2$. Decomposition was found to begin at 230° C, and conversion to the oxide was complete at 680° C. These workers also quote the decomposition temperature of zirconium selenite as 537° C, but no details are given.

METHOD

PREPARATION OF PRECIPITATE—

Prepare stock solutions of pure zirconyl chloride ($ZrOCl_2.8H_2O$) and of pure hafnyl chloride ($HfOCl_2.8H_2O$) in N hydrochloric acid. Spectrographic analysis of our hafnium solution showed that it contained 0·9 per cent. of zirconium (as zirconia).

The selenites were prepared by Claasen's procedure as described below.

Transfer 25 ml of the appropriate stock solution to a 400-ml beaker, and add sufficient N hydrochloric acid to give a final acidity of 0·3 N when diluted to 200 ml. Effect precipitation by adding to the cold stock solution a freshly prepared and filtered 10 per cent. w/v solution of selenous acid, with stirring; then raise the temperature to about 90° C. Maintain this temperature for about 24 hours by standing the beaker over a low bunsen flame, after which time conversion to the crystalline normal selenite should be complete.

The completeness of the conversion can be judged visually, as the normal selenite is crystalline, has less volume and settles rapidly after agitation; the basic selenite is a bulky

gelatinous precipitate and settles only slowly. In general, the time taken for the conversion of the hafnium compound is 2 to 3 hours less than that required for the zirconium compound.

Decant the hot supernatant liquid through a porous porcelain crucible. Wash the precipitate in the beaker with hot water, and decant the washings through the crucible. This procedure was repeated many times until all of the precipitate had been transferred to the crucible. Then wash the precipitate in the crucible with cold water until the washings are free from selenous acid.

Carefully wipe the outside of the crucible, place it in a desiccator and set it aside overnight before examination in the thermobalance.

THERMOGRAVIMETRIC EXAMINATION—

A Stanton recording thermobalance was used for the thermogravimetric examination of the precipitates. The sensitivity of this particular instrument was 0·1 mg, and the platinum-wound furnace gave a maximum temperature of 1420° C. Both the temperature and the weight were recorded on a single chart, each scale being about 5 inches wide. The temperature scale was calibrated between 0° and 1500° C, each division representing 10° C. The weight scale covered a range of 10 mg, each division representing 0·1 mg.

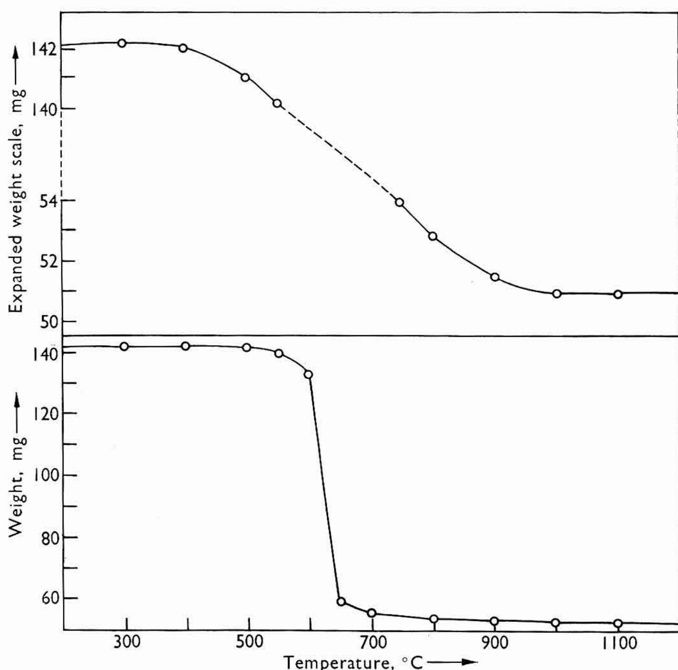

Fig. 1. Typical decomposition curve for zirconium selenite

The temperature of the furnace was closely controlled to give a linear heating-rate of approximately 6·7° C per minute. In all, about $3\frac{1}{2}$ hours were required to reach 1200° C from cold. This upper limit of 1200° C was imposed because of the possible deterioration of the glaze on the crucibles at higher temperatures.

THE BUOYANCY EFFECT—

An empty crucible, when heated in the furnace, apparently increases in weight. This is owing to the furnace atmosphere becoming less buoyant as its density decreases. The extent of this apparent change in weight is dependent on the size of the crucible, the rate of heating and the temperature range used. For the 00/A1 crucibles used in this work, an increase of 5 to 6 mg was recorded between 100° and 1200° C. The rate of change, although not quite linear, was approximately 0·4 mg per 100° C rise in temperature.

To avoid possible cumulative errors, each crucible was tared by heating in the furnace whilst recording its weight continuously over the temperature range to be employed in the examination of the precipitate. After repeating the procedure with the loaded crucible, the net weight at any temperature was determined as the difference between the gross weight and the tare weight.

It is from these derived results that the weight - temperature graphs were drawn.

It has been suggested[7] that a better correction for buoyancy would be obtained by heating the crucible with an equivalent volume of inert material of the same density through the temperature range. It was felt that, with the small samples used in this work, no appreciable benefit would be gained by using such a procedure.

RESULTS

Typical decomposition curves for the normal selenites of zirconium and hafnium are shown in Figs. 1 and 2, from which the facts detailed below were deduced.

ZIRCONIUM SELENITE—

The weight remained constant up to 400° C after which a steady though small loss occurred up to 550° C. This amounted to approximately 1 mg from 140 mg of sample. Between 530° and 650° C decomposition was rapid, the loss over this range being about 80 mg. Although the weight became almost constant at 650° C, there was a small loss up to 1000° C, above which the weight was constant. The loss during this phase was about 2 mg (see Fig. 1).

The molecular weight of the precipitate, calculated from the weight of the zirconia obtained, agreed well with the formula $Zr(SeO_3)_2$, as shown in Table I.

TABLE I

MOLECULAR WEIGHT OF ZIRCONIUM SELENITE CALCULATED FROM WEIGHT OF ZIRCONIA IN IGNITED PRECIPITATE

Weight of precipitate, mg	Weight of zirconia obtained, mg	Molecular weight— calculated	theoretical
71·3	25·0	351·4	345·14
142·1	50·9	344·0	
137·0*	51·2	329·6	

* Conversion to the normal selenite was incomplete; this was demonstrated by the fact that filtration was more difficult and that the decomposition curve was different from the others (*viz.*, the weight below 250° C was never quite constant, and above 250° C decomposition occurred, 10 mg being lost by the time 550° C was reached).

TABLE II

MOLECULAR WEIGHT OF HAFNIUM SELENITE CALCULATED FROM WEIGHT OF HAFNIA IN IGNITED PRECIPITATE

Weight of precipitate, mg	Weight of oxide obtained, mg	Molecular weight— calculated	corrected*	theoretical
79·1	38·1	437·0	435·5	432·4
122·9	60·1	430·5	428·9	
121·7	58·6	437·2	435·6	

* Corrected for the presence of 1 per cent. of zirconium dioxide in the hafnium oxide.

HAFNIUM SELENITE—

The decomposition curve, see Fig. 2, was similar to that of zirconium selenite, although displaced along the temperature axis by some 100° C. The compound was stable up to 500° C and between this temperature and 600° C there was a small loss amounting to 0·5 mg on a 120 mg sample. Between 600° and 750° C there was rapid decomposition, the weight loss in this range being about 60 mg. Above 750° C the loss in weight was slight, amounting to about 3 mg up to 1000° C. Above 1000° C the weight was constant, conversion to the oxide being complete.

The calculated molecular weight of the precipitate showed close agreement with the theoretical molecular weight of $Hf(SeO_3)_2$, as shown in Table II.

MIXED ZIRCONIUM - HAFNIUM SELENITES—

The decomposition curves for the mixed selenites of hafnium and zirconium were similar to those for the individual compounds. The results obtained from the curves permit the hafnium and zirconium contents of the original mixture to be determined, as shown in Table III.

TABLE III

RESULTS FOR DETERMINATION OF OXIDE CONTENTS IN A MIXTURE OF HAFNIUM AND ZIRCONIUM SELENITES

Weight of mixed selenites, mg	Weight of mixed oxides, mg	Hafnium oxide found, %	Hafnium oxide calculated, %
131·8	54·4	55·05	53·5
132·2	54·5	54·7	

DISCUSSION OF RESULTS

The composition of the precipitated zirconium and hafnium selenites, calculated from the above results, shows good agreement with the theoretical requirements of the formulae $Zr(SeO_3)_2$ and $Hf(SeO_3)_2$ for the normal selenites. The behaviour during ignition is similar, except that the hafnium compound decomposes at a temperature some 100° C higher than that of the zirconium compound.

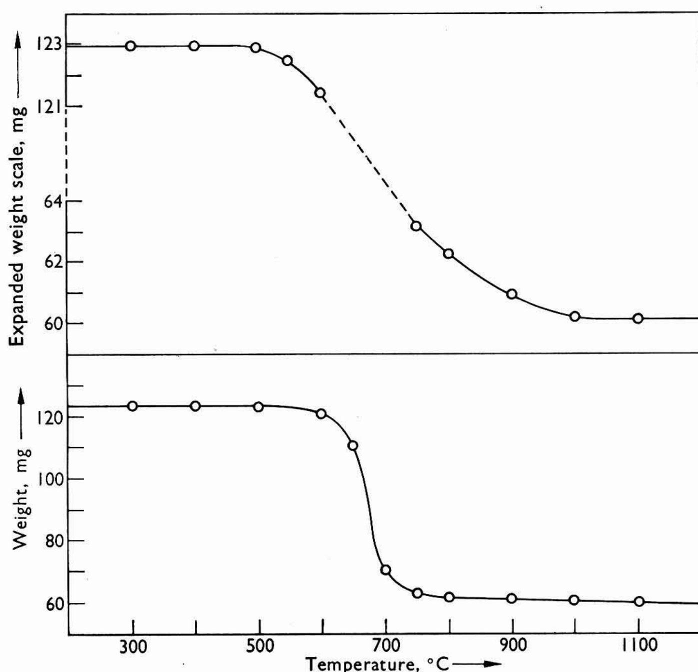

Fig. 2. Typical decomposition curve for hafnium selenite

Comparison between these results and those obtained by Duval and his co-workers is not easy for several reasons. No mention is made in their paper on zirconium compounds[5] of the hafnium content of their zirconium source, although it is stated that some precipitates were prepared from pure zirconyl chloride and others from commercial zirconyl chloride. Unfortunately, however, there is no indication in the text of the sources of the individual precipitates, thus making an assessment of the calculated molecular weights difficult.

The behaviour of their basic zirconium selenite is similar to that of the zirconium selenite giving the result marked with an asterisk in Table I, for which it was obvious that conversion to the normal selenite had been incomplete. This is true both for the apparent molecular weight and for the behaviour during ignition. The isolated fact quoted in their subsequent report,[6] that normal zirconium selenite begins to decompose at 557° C, agrees with the result obtained here for the rapid decomposition of this compound.

The result obtained for the decomposition of normal hafnium selenite by Dautel and Duval,[6] that decomposition begins at 230° C, differs considerably from the temperature of 500° C (600° C for rapid decomposition) given above. By comparison of Dautel and Duval's decomposition curve with that of the asterisked result in Table I, it would appear that conversion of their precipitate to the normal selenite was incomplete, although not sufficiently so to cause an appreciable error in the calculated molecular weight.

Further, the small loss in weight both before and after the rapid decomposition does not appear to have been recorded by Dautel and Duval. From a description of the Chevenard thermobalance,[8] the sensitivity appears to be such that this small loss of weight (*i.e.* ± 1 mg) should have been recorded. However, if no correction was made for buoyancy changes, then it seems probable that apparent gain in weight due to this effect would compensate for this small weight loss, thus giving a record of constant weight. It is ironic that the upper temperature reached by these workers was 1000° C, since it is at this temperature that the error should have become apparent.

Conclusions

The procedure developed by Claasen[3] appears to be excellent, provided that sufficient care is taken to ensure that the conversion from the basic selenite to the normal selenite is complete. The upper temperature limit for drying zirconium selenite before direct weighing is 400° C and that for hafnium selenite is 500° C. If the salts are to be ignited to the oxides, then a minimum temperature of 1000° C is necessary.

Since the temperature ranges of decomposition for the two salts overlap considerably, there is no possibility of determining the ratio of zirconium to hafnium directly from the thermogram. This ratio can, however, readily be determined by weighing the mixed selenites, and then, after ignition, weighing the oxides.

From these conclusions, the caution advocated in one of the recent authoritative texts on analytical methods[9] in the use of selenous acid for the determination of zirconium would appear to be unnecessary.

We thank Dr. J. S. Fletcher of Magnesium Elektron Ltd. for gifts of zirconyl and hafnyl chlorides and for their spectrographic analysis.

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The Emission-spectrographic Determination of Impurities in Uranium-233 Dioxide after Pre-concentration of the Rare-earth Elements by Ion Exchange

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Twenty-nine impurity elements are measured directly in uranium-233 dioxide by the carrier-distillation method. Enhancement of some of these impurity elements (magnesium, bismuth, antimony, lead, manganese, zinc, cadmium and indium) in the uranium dioxide matrix is shown. The precision of the carrier-distillation method is improved by using internal standard control. Rare-earth elements are determined by a spectrographic method after concentration by ion exchange, giving a total of 45 impurity elements determined for each sample. The uranium-233 is recoverable after the analysis.

PURE uranium-233 dioxide, prepared from neutron-irradiated thorium-232, was required for the measurement of neutron total cross-section over the energy range 30 eV to 60 KeV. Complete analysis for impurities was necessary, particularly for those elements having large neutron-capture cross-sections, and for which the upper permissible limit was at the part per million level. The amount of sample available for the analysis was limited to about 2 g; consequently, general spectrographic methods were considered, since they give much information on a small sample.

Because of the radioactivity of the sample, all operations had to be adaptable to permit working in a glove-box.

PRELIMINARY CONSIDERATIONS—

The carrier-distillation method[1] can be applied directly to refractory oxides without further treatment; it is known that about 29 volatile impurity elements can be analysed with a high degree of sensitivity, but generally with rather poor precision. Since it is known that internal standard control usually gives improved precision, this procedure could be used in the work described here. However, this method could not be used for determining impurities that form refractory oxides, including the important neutron-absorbing rare-earth elements. Since these elements are also insensitive in direct spectrographic methods, particularly in the presence of the complex uranium spectrum, a preliminary chemical separation from the uranium may be necessary. Uranium could be removed by chromatographic separation as uranyl nitrate, $UO_2(NO_3)_2$,[2,3] the rare-earth elements being held on a cellulose chromatographic column while the uranium passes through in ether - nitric acid solution. The column material may then be ashed, finally purified and then measured spectrographically. A quicker and less hazardous procedure for glove-box work would involve removal of the uranium by anion exchange from a chloride medium[4]; the rare-earth elements may then be precipitated on a suitable carrier directly from the column eluate without further purification. The individual rare-earth elements could then be determined spectrographically by the iron-flux method.[5,6]

THE DETERMINATION OF ELEMENTS OTHER THAN RARE EARTHS—

The matrix in the carrier-distillation method for determining impurities in uranium is usually U_3O_8. Since the samples in this work were in the form of hydrogen-reduced uranium dioxide, it was considered preferable to use this compound for the excitation rather than risk losing volatile impurities during a preliminary ignition to U_3O_8 in air. This was considered feasible since Marinkovic[7] has, in fact, shown that U_3O_8 is reduced to uranium dioxide at the high temperature of the carrier-distillation arc in a graphite electrode.

PROCEDURE—

Grind 6·80 mg of Specpure cobalt oxide with 100 mg of gallium oxide. Grind 6·41 mg of this mixture with 294 mg of uranium dioxide to give 1000 p.p.m. of cobalt in the electrode

charge. This provides a cobalt line at 2541·4 Å and a line from the gallium carrier at 2624·8 Å, for use as the internal standards. Weigh 100-mg portions into each of three Scribner - Mullin type graphite electrodes.

Expose the plate under the conditions listed below—

Spectrograph:	Hilger quartz Littrow.
Wavelength range:	2450 to 3500 Å.
Slit width:	0·015 mm.
Condenser lens:	Quartz, *f* 15 cm; placed 58 cm from the slit of the spectrograph.*
Lower electrode:	Anode. NCC graphite, Scribner - Mullin type,[1] pre-burned for 30 seconds, at 10 amperes before filling.
Upper electrode:	Cathode. NCC graphite, 3·2 mm in diameter, flat end.
Arc gap:	4 mm.
Arc current:	10 amperes.
Exposure:	Pre-arced for 5 seconds with shutter closed, then exposure recorded for the duration of the gallium emission *plus* 5 seconds (total time ~40 seconds).
Photographic plate:	Ilford Ordinary.

The analytical lines and the corresponding detection limits for many elements are shown in Table I. Cobalt is measured by the line at 2521·4 Å (with a sensitivity of 4 p.p.m.) in separate exposures on a sample without added cobalt as internal standard.

TABLE I

ANALYTICAL LINES AND LIMITS OF DETECTION OF IMPURITIES IN URANIUM BY THE CARRIER-DISTILLATION METHOD

Impurity element	Wavelength, Å	Detection limit, p.p.m.	Impurity element	Wavelength, Å	Detection limit, p.p.m.
Aluminium	3082·2	1	Molybdenum	3132·6	2
Silver	3280·7	0·2	Nickel	3050·8	1
Arsenic	2860·5	10	Phosphorus	2535·7	8
Gold	2676·0	0·5	Lead	2802·0	1
Boron	2496·8	0·5	Palladium	3242·7	10
Beryllium	3130·4	0·3	Antimony	2598·1	5
Bismuth	3067·7	0·5	Silicon	2881·6	5
Cadmium	3261·1	7	Tin	3034·1	0·5
Chromium	2835·6	1	Titanium	3234·5	300
Copper	3247·5	2	Thallium	2767·9	0·3
Iron	2599·6	2	Vanadium	3184·0	5
Germanium	2651·2	0·4	Tungsten	2947·0	150
Indium	3256·1	1	Zinc	3345·0	20
Magnesium	2802·7	2	Cobalt*	2521·4	4
Manganese	2576·1	0·5	Gallium*	2624·8	carrier

* Internal standard lines.

TABLE II

EFFECT OF INTERNAL-STANDARD CONTROL ON PRECISION

Line pair element - internal standard, Å	Coefficient of variation, based on 12 replicates at 100 p.p.m.: On intensity ratios, %	On element line minus background, %
B 2496·8 - Ga 2624·8	7	11
Pb 2802·0 - Ga 2624·8	6	18
In 3256·1 - Ga 2624·8	4	16
Sn 2863·3 - Ga 2624·8	14	29
Mn 2801·1 - Co 2521·4	7	12
Fe 2599·6 - Co 2521·4	10	16
V 3184·0 - Co 2521·4	13	19
Mg 2802·7 - Co 2521·4	14	19

* This lens was necessary because of our glove-box and spectrograph arrangement. If the source can be placed 38 cm from the slit, no lens is necessary.

The improvement in the precision obtained by using internal standard control is shown in Table II for some of the analytical line pairs that are employed. Internal standard control also gives much greater plate-to-plate consistency than can be obtained by using ratios with the adjacent backgrounds.

Since existing standards and standard plates were based on a U_3O_8 matrix, the effect of the different uranium matrices, uranium dioxide and U_3O_8, on the emission spectra of impurities was studied. Additions of 50 and 200 p.p.m. of each of the elements listed in Table I were made to pure matrices of uranium dioxide and U_3O_8, and spectrograms were taken of these together with blank determinations on the pure matrices. The results obtained with the uranium dioxide matrix in comparison with the normal U_3O_8 matrix, were—

Impurity elements whose line intensities were enhanced: magnesium, bismuth, antimony, lead, manganese, zinc, cadmium and indium.

Impurity elements whose line intensities were unchanged: silicon, boron, tin, gallium, chromium, aluminium, nickel, silver and iron.

Impurity elements whose line intensities were suppressed: gold, vanadium, arsenic, thallium, germanium, molybdenum, beryllium, palladium, copper and cobalt.

Some elements show an increase of sensitivity in the uranium dioxide matrix, in agreement with the findings of Marinkovic[8]; in others there is a reduction in sensitivity. Molybdenum is suppressed in the uranium dioxide to an exceptional extent, and the reason for this was investigated. It was shown that reduction of the molybdenum trioxide impurity takes place under the strongly reducing conditions occurring in the graphite electrodes that contain uranium dioxide, giving a relatively non-volatile reduction product. U_3O_8 on the other hand supplies oxygen to the system and prevents this reduction; the molybdenum is therefore vaporised as the volatile molybdenum trioxide. These results are to be reported fully elsewhere.[9]

Because of this difference in behaviour of impurities in the two matrices, spectrographic standards for the work described here had to be prepared in a matrix of pure uranium dioxide. Confirmation of the levels of the non-volatile impurity elements in the samples of uranium-233 was obtained by repeating the carrier-distillation procedure on a portion of each sample of uranium-233 after ignition to U_3O_8 in air at 780° C for half an hour. The direct examination of the uranium dioxide matrix, however, ensured that there was no risk of ignition losses of the more volatile impurity elements.

Determination of rare-earth elements

The optimum concentration of hydrochloric acid solution for the retention of uranium on De-Acidite FF ion-exchange resin is about 8 M.[10] At this concentration few impurity elements are retained, and most are eluted by passing several column-volumes of 8 M hydrochloric acid.

Fine particles must be removed from the resin, since any uranium that is retained on them might be carried down the column during the subsequent elution of the rare-earth elements. They are removed by a preliminary washing, by decanting the resin and by a further washing of the prepared columns. A slight yellow colour may be observed in the first portion of 8 M hydrochloric acid eluted from the column, but this is due to organic matter and may be ignored, since it has been shown in this work to contain no uranium.

The iron-flux method[5] is used for measuring the individual rare-earth elements in the concentrate from ion-exchange separation. In this method the matrix containing the rare-earth elements is a fused bead of ferric oxide on a copper electrode, so the spectrum obtained is principally that of iron superimposed on copper. The line intensities produced by the rare-earth elements are measured relative to those of iron, which serves as the internal standard.

Preparation of the columns—

Wash the De-Acidite FF exchange resin, sieved to 100 to 200 mesh, by decanting with water to free it from fine particles, and then purify it by successive washes in 75, 50, 25, 10, 5 and 1 per cent. v/v solutions of hydrochloric acid, sp.gr. 1·18, in water. Store in deionised water until required for use. Make the columns from polythene tubes 20 cm long and 1·3 cm in diameter, with the bottom end drawn to a capillary to control the flow rate to about 1 ml per minute and the top end welded to a polythene funnel for ease of filling. Prepare the columns by pouring a slurry of 33 ml of wet resin onto a silica-wool plug at the

bottom of the column, and pre-wash this resin with successive 50-ml portions of hydrochloric acid (1 + 1), hydrochloric acid, sp.gr. 1·18, 0·1 M hydrochloric acid, hydrochloric acid (1 + 1) and finally with 50 ml of hydrochloric acid, sp.gr. 1·18. Prepare the hydrochloric acid used for the final washings by dissolving cylinder hydrochloric acid gas in ice-cold de-ionised water; standardise this solution by measuring the specific gravity at 20° C in a pycnometer.

SEPARATION PROCEDURE—

Dissolve an amount of the uranium dioxide sample equivalent to 0·5 g of uranium by warming it in a silica beaker with 10 ml of hydrochloric acid, sp.gr. 1·18, and five drops of nitric acid, sp.gr. 1·42. (Any small insoluble residue is separately examined spectrographically for rare-earth elements.) Transfer the solution to the prepared ion-exchange column, rinse the beaker with 8 M hydrochloric acid, and add the rinsings to the column. Elute the impurities with 130 ml of 8 M hydrochloric acid, and collect the eluate in a 250-ml Pyrex glass beaker. (A precipitation carried out in a fused silica beaker showed a tendency for the ferric hydroxide to stick to the beaker surface; radioactive daughters from the uranium-233 were also strongly adherent. This difficulty was avoided by using Pyrex beakers in subsequent runs.)

Boil the eluate to reduce the volume to about 75 ml, add 10 mg of Specpure ferric oxide in 1 ml of M hydrochloric acid, and then co-precipitate the rare-earth elements on ferric hydroxide by adding an excess of ammonia solution, sp.gr. 0·88. (The ammonia solution should be of B.D.H. Foodstuffs Analysis grade and should be from a recent batch, otherwise the precipitate may be contaminated by silica.) Digest the precipitate on the hot-plate for 30 minutes, and then set it aside overnight. Filter off the precipitate on an 11-cm Whatman No. 541 filter-paper, wash with hot 1 per cent. v/v ammonia solution, dry, and ignite it at 800° C to constant weight in a silica crucible. Strip off the uranium from the ion-exchange column for recovery, by washing with 80 ml of 0·1 M hydrochloric acid. The column may then be used again.

SPECTROGRAPHIC MEASUREMENT OF THE CONCENTRATES—

Grind the concentrate, precipitated on 10 mg of ferric oxide, in an agate mortar with 40 mg of Specpure ammonium sulphate. Press this mixture in a steel die into pellets $\frac{1}{8}$ inch in diameter, each weighing 9 to 11 mg. Examine these pellets spectrographically under the conditions listed below—

Spectrograph:	Hilger quartz Littrow.
Wavelength range:	2750 to 4750 Å.
Slit:	0·015 mm × 1·5 mm.
Condenser lens:	None.
Arc gap:	3 mm.
Arc current:	7 amperes.
Upper electrode:	Anode. Specpure copper, 7 mm in diameter, 80° cone.
Lower electrode:	Cathode. Specpure copper, 5 mm in diameter, flat top.
Exposure:	45 seconds, after pellet begins to burn.
Photographic plate:	Ilford Ordinary.

Since radioactive daughters of uranium-233 are present, carry out the excitation of the concentrates from the uranium in a totally enclosed arc chamber[11] that is exhausted through a filter. Initiate the d.c. arc by a remotely controlled electronic triggering device.[12]

Record 3 or 4 exposures of each sample concentrate, together with six standards prepared by diluting Specpure rare-earth oxides with a mixture of equal parts by weight of pure ferric sulphate and ammonium sulphate. Avoid over-complication of the standard spectra, by dividing the standards into two separate series, A and B, containing dilutions of the elements listed below—

Series A: europium, cerium, terbium, holmium, gadolinium, lutetium, erbium and ytterbium.

Series B: scandium, yttrium, lanthanum, dysprosium, neodymium, samarium and praseodymium.

Measure the densities of the rare-earth element lines and of the corresponding iron internal standard lines shown in Table III and, after subtracting the adjacent backgrounds, evaluate the intensity ratios on a Respektra calculating board.[13] Read off the concentration of each rare-earth element from the calibration curves obtained from the standard mixtures.

Results

The detection limits that are obtained when 0·5 g of uranium is used as starting material are shown in Table III.

Table III

Rare-earth element line pairs and detection limits

Impurity line, Å	Internal standard line, Å	Index point, per cent. in flux	Detection limit in 0·5 g of uranium, p.p.m.
Dy 3461·0	Fe 3458·3	0·14	7
Sm 3670·8	Fe 3674·8	0·046	20
Eu 2814·0	Fe 2815·5	0·037	5
Gd 3032·9	Fe 3045·1	0·26	7
Yb 2891·4	Fe 2887·8	0·030	5
Lu 2847·5	Fe 2846·8	0·072	7
Ho 3515·6	Fe 3516·4	0·086	10
Tb 3561·7	Fe 3560·7	0·075	5
Er 3692·7	Fe 3668·9	0·0096	7
Sc 3015·4	Fe 3017·6	0·58	2
Nd 4012·3	Fe 4018·3	0·040	5
La 3303·1	Fe 3303·6	0·035	10
Y 3203·3	Fe 3202·6	0·022	2
Pr 4179·4	Fe 4208·6	0·057	7
Tm 3131·3	Fe 3151·4	0·075	2
Ce 4572·3	Fe 4581·5	0·13	7

Silica was found in the ferric hydroxide precipitates; it probably originated from the ammonia solution and from glassware. It was shown from earlier work that the presence of silica in the iron-flux pellets could result in the suppression of the intensity of some elements owing to the formation of non-volatile silicates. To investigate the possible effect of this on the rare-earth elements, a 1 per cent. addition of silica was made to a standard mixture, and the intensity ratios that were obtained from this mixture were compared with those from the original standard.

The results of these measurements are shown in Table IV, in which each value is the mean of three replicates.

Table IV

Effect of silica on intensity ratio

Element	Ratio— in absence of SiO_2	with 1 per cent. of added SiO_2
Holmium	0·616	0·640
Lutetium	0·596	0·596
Ytterbium..	1·34	1·40
Terbium	0·630	0·624
Erbium	2·09	2·33

Since the silica content of the precipitate is usually well below 1 per cent., it is concluded that it has no serious effect on the measurements.

The efficiency of the co-precipitation of the rare-earth elements on ferric hydroxide was assessed by using cerium-141 - cerium-144 radioactive tracer. Four microcuries of the cerium tracer solution were brought into equilibrium with 200 μg of inactive cerium carrier by oxidation with nitric acid and hydrogen peroxide, and then by reduction to cerium^{III} with hydroxylammonium chloride. Portions (20 μg) of this labelled cerium were co-precipitated with 10 mg of ferric oxide as the hydroxide, which was then ignited as described in the procedure and the activity measured by β-counting. As a control, the same amount of tracer was poured as a slurry directly on 10 mg of ferric oxide on a counting tray. The precipitation recoveries of two such experiments were—

Experiment	1	2	Control
Activity, β-counts per minute per mg ..	393	412	409

The mean value from the two experiments was 403 β-counts per minute per mg, which corresponds to a recovery of 99 per cent. of the amount of cerium taken.

The same tracer solution was used for measuring the recovery of cerium during the ion-exchange separation of rare-earth elements from 0·5 g of natural uranium. One portion of tracer was first reduced to cerium^{III} with hydroxylammonium chloride and a second was oxidised to cerium^{IV} with hydrogen peroxide. The cerium^{III} and cerium^{IV} tracers were then added to separate 0·5-g portions of natural uranium, and the rare-earth separations were carried out as described in the procedure. The concentrates that were obtained on ferric oxide were each counted to determine the recoveries of cerium^{III} and cerium^{IV} respectively. Controls for both cerium^{III} and cerum^{IV} in the absence of uranium or without ion-exchange treatment were precipitated directly on ferric hydroxide to provide reference standards.

β-Counting of the concentrates on ferric oxide revealed the presence of uranium daughters that had separated on the columns into the concentrates and that interfered with the count of the cerium tracer. The determinations were therefore made by counting the 0·145-MeV cerium-141 and 0·134-MeV cerium-144 γ-ray peaks on a 100-channel γ-ray spectrometer. Direct measurements on the natural uranium at the position of these peaks showed that there was no interference from the uranium daughters on the peaks. The recoveries obtained were 97 per cent. for cerium^{III} and 95 per cent. for cerium^{IV}.

Recoveries of the other rare-earth elements were assessed spectrographically by separation runs starting with known additions of 40 p.p.m. of the individual pure rare-earth elements to solutions in hydrochloric acid of both pure natural uranium and the uranium-233. The separated rare-earth elements were measured spectrographically by the method given above and the recoveries obtained are shown in Table V.

TABLE V

RECOVERIES OF KNOWN ADDITIONS AFTER ION-EXCHANGE SEPARATION

Element	Amount recovered, per cent.	Element	Amount recovered, per cent.
Dysprosium	70	Scandium	108
Europium	90	Neodymium	70
Gadolinium	83	Lanthanum	82
Ytterbium	80	Yttrium	91
Lutetium..	71	Praseodymium	104
Holmium..	95	Samarium	100
Terbium	87	Thulium	100
Erbium	85		

Although the recoveries of the individual rare-earth elements range from 70 to 108 per cent., these values were considered to be adequate for the analytical requirements of this work.

No significant amounts of rare-earth elements were found in the uranium-233 samples proposed for the cross-section measurements; in each experiment the concentrations were found to be below the limits of detection set out in Table III. The elements lead, iron, aluminium and silicon were found in amounts exceeding 100 p.p.m.; other elements were found in amounts below this level or were not detected at the levels listed in Table I.

The uranium-233 can be recovered completely after the analysis, since it is not consumed in the carrier-distillation process and it is stripped off from the ion-exchange columns after the separation of rare-earth elements have been carried out.

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Determination of Traces of Iron and Lead in Copper Metal and Cupric Salts

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Methods are described for the colorimetric determination of trace amounts of iron and lead in high-purity copper metal and analytical-reagent grade cupric salts. Copper is separated by precipitation of cuprous thiocyanate from homogeneous solution, and the iron and lead, which remain in the filtrate, are determined with 4,7-diphenyl-1,10-phenanthroline and dithizone, respectively.

SENSITIVE colorimetric reagents for iron, such as 2,2'-dipyridyl and 1,10-phenanthroline and its derivatives, react also with copper. Dithizone, which is the most popular sensitive reagent for lead, also reacts with copper.

Consequently, if these reagents are to be used for determining microgram amounts of iron or lead in materials containing relatively large amounts of copper, the iron or lead must either be separated from the copper before making the colorimetric determination, or the copper must be masked during the determination.

Thus, for the determination of iron, copper can be first removed by controlled-potential electrolysis[1,2] or by precipitation as cuprous thiocyanate.[3] Alternatively, the iron can be removed by co-precipitation as ferric hydroxide with hydrated manganous oxide[3] and aluminium hydroxide,[4] or by precipitating metallic iron on pure cadmium.[5] A high concentration of cyanide can be used to mask cuprous copper when determining traces of iron in copper metal with 4,7-diphenyl-1,10-phenanthroline.[6]

Analogous procedures have been described for determining traces of lead. The copper can be removed by electrolysis.[2,7] Lead can be separated by co-precipitation with ferric hydroxide[8] and barium chromate[9]; and copper can be masked with cyanide.[10,11]

Procedures for co-precipitating iron or lead are tedious, multi-stage processes that are inclined to give high blank values. Methods in which appreciable concentrations of cyanide are used as a masking agent also have disadvantages; in the iron determination with 4,7-diphenyl-1,10-phenanthroline, the calibration standards must be prepared in the presence of iron-free copper[6]; and the cyanide used in the determination of lead with dithizone, must be free from traces of sulphide,[10] which is a fairly common impurity.

Precipitation from homogeneous solution produces insoluble compounds that are less contaminated than those produced by conventional methods of precipitation with substances that are not isomorphous with the precipitate.[12] It was decided, therefore, to examine the recently reported precipitation from homogeneous solution of cuprous thiocyanate,[13] as an alternative to electrolysis for separating copper from traces of iron and lead.

EXPERIMENTAL

CONVENTIONAL PRECIPITATION—

Zharovskiĭ[3] reported that traces of iron could be determined in copper after removal of the copper by a conventional precipitation of cuprous thiocyanate with sulphite as the reducing agent.[1] However, results obtained by Diehl and Buchanan[6] indicated that small amounts of iron are co-precipitated with cuprous thiocyanate. We decided, therefore, to examine the conventional precipitation as a means of separating copper.

Accordingly, four 50-ml portions of 2 per cent. w/v solution of cupric sulphate were taken, and known amounts of iron and lead were added to three of them. After acidification and dilution to 100 ml with water, the copper was precipitated from each solution by using the conventional precipitation procedure described by Vogel.[16] After filtration, portions of each filtrate were tested for iron and lead by using the methods described below. The results, which are given in Table I, show that this procedure is unsuitable for the determination of p.p.m. amounts of iron and lead. No further determinations were attempted in this way.

Precipitation of cuprous thiocyanate from homogeneous solution is achieved by adding hydroxylammonium chloride to a solution containing cupric and thiocyanate ions, and heating.

The filtrate contains about 0·4 μg of copper per ml.[13] Since the filtrate contains an excess of reducing agent, it was decided to use a reagent for ferrous iron. Bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) was chosen for this purpose; it is one of the most sensitive reagents for iron, and its reaction with iron is not affected by the presence of thiocyanate or by the amount of copper that remains in the filtrate after the precipitation of cuprous thiocyanate.[14] The procedure chosen for the iron determination was essentially that of Smith, McCurdy and Diehl,[15] except that chloroform was used to extract the ferrous bathophenanthroline complex.[14]

The determination of lead was carried out with dithizone and was based on the method of Silverman,[10] except for two modifications. Much less cyanide was added to the test solution because only a trace of copper was present, and the first dithizone extraction was made with stronger dithizone solution than that used for the final colorimetric measurement, as it was found that this facilitated the extraction of lead.

TABLE I

DETERMINATIONS OF IRON AND LEAD AFTER CONVENTIONAL PRECIPITATION OF CUPROUS THIOCYANATE

1 g of $CuSO_4.5H_2O$ was taken for each test

Iron added, μg	Iron found, μg	Lead added, μg	Lead found, μg
0	0·25	0	10·0
5	3·5	5	9·6
10	6·8	5	8·6
5	3·8	10	13·4

PRECIPITATION FROM HOMOGENEOUS SOLUTION—

Precipitation of cuprous thiocyanate was carried out from solutions containing 1 g of the salt being tested or, when the raw material was copper metal, from solutions containing up to 0·25 g of copper. Solutions of copper metal were prepared by dissolving the appropriate weight of copper in a mixture of equal volumes of nitric acid, sp.gr. 1·42, and water. When solution was complete, sufficient sulphuric acid, sp.gr. 1·84, was added to produce a solution with an acidity equivalent to 0·25 N sulphuric acid. The solution was then heated until fumes appeared, cooled, treated with water, heated again until fuming and then cooled and diluted to the required volume with water.

REAGENTS—

Ammonium thiocyanate solution—7 per cent. w/v in water.

Hydroxylammonium chloride solution—6 per cent. w/v in water.

NOTE—When lead is subsequently to be determined, it is advisable to purify each of these reagents as follows. Prepare a solution approximately twice the strength required. Note the pH, and then adjust it to pH 9 by the addition of ammonia solution. Transfer the solution to a separating funnel and extract it with small quantities of a 0·02 per cent. solution of dithizone in chloroform, discarding the organic phase after each extraction, until two successive extracts remain green. Adjust the pH of the solution to its original value by adding sulphuric or hydrochloric acid, and then extract the solution with small amounts of chloroform, discarding the chloroform layer after each extraction, until two successive extracts remain colourless. Dilute the solution with water to the required strength.

METHOD—

Transfer the solution containing copper to a clean, unscratched 200-ml Phillips beaker and dilute to 100 ml with water. Add dilute sulphuric acid, if necessary, to give a sulphuric acid concentration between 0·2 and 0·3 N. Add 15 ml of ammonium thiocyanate solution, mix and add 15 ml of hydroxylammonium chloride solution. Mix, and heat on a steam-bath for 45 minutes. Cool the solution to room temperature, set aside for 10 minutes and filter through a medium-porosity sintered-glass crucible. Take suitable portions of the filtrate for the determinations of iron and lead.

Prepare a blank solution using the same quantities of the reagents. It is not necessary to heat the blank solution.

Determination of iron

Reagents—

All reagents should be of analytical-reagent grade unless otherwise specified.

Ascorbic acid solution—Dissolve 10 g of ascorbic acid in 100 ml of water. This solution should be freshly prepared.

Sodium acetate solution—Dissolve 10 g of hydrated sodium acetate in 100 ml of water.

Bathophenanthroline solution, 0·001 M—Dissolve 0·0332 g of 4,7-diphenyl-1,10-phenanthroline in 100 ml of ethanol.

Chloroform.

Ethanol—Industrial methylated spirit, 74° O.P.

Standard iron solution—Dissolve 8·65 g of ammonium ferric sulphate in 50 ml of nitric acid, sp.gr. 1·42, and add sufficient water to produce 1 litre.

1 ml ≡ 1 mg of iron.

Dilute standard iron solution—Dilute 10 ml of the standard iron solution to 1 litre with water; this solution must be freshly prepared before use.

1 ml ≡ 10 μg of iron.

Preparation of calibration graph—

Measure amounts of dilute standard iron solution to cover the range 0 to 40 μg of iron into separate 150-ml separating funnels. Dilute each portion with 20 ml of water, add 5 ml of ascorbic acid solution and 5 ml of sodium acetate solution, and adjust the pH to between 4 and 6, if necessary, by dropwise addition of hydrochloric acid or ammonia solution. Add 10 ml of bathophenanthroline solution, and set aside for 5 minutes. Add 5 ml of chloroform, insert the stopper, shake the funnel vigorously for 30 seconds, and allow the layers to separate. Run the chloroform layer through a glass-wool plug, supported in a small funnel, into a 25-ml calibrated flask containing a few millilitres of ethanol. Add another 5 ml of chloroform to the contents of the separating funnel, extract by shaking for a few seconds, allow the layers to separate, and add the second chloroform extract to the first.

Dilute the combined extracts to the mark with ethanol, mix, and measure the optical density at 533 mμ in a 1-cm cell, against the solution containing no added iron. The graph relating optical density to amount of iron present should be linear and pass through the origin.

Method—

Transfer a portion of the filtrate resulting from precipitation of the cuprous thiocyanate (p. 42), and containing not more than 40 μg of iron, to a separating funnel. Add 5 ml of ascorbic acid solution and 5 ml of sodium acetate solution, and adjust the pH of the solution to between 4 and 6, if necessary, by adding ammonia solution. Add 10 ml of bathophenanthroline solution, and complete the determination as described under "Preparation of Calibration Graph." Prepare the reference solution from the blank solutions used on the precipitation reagents.

Results—

Solutions were prepared from 0·25 g samples electrode copper-rod (Johnson Matthey & Co. Ltd.) containing 1 p.p.m. of iron, according to the suppliers spectrographic analysis. Iron was added to three of these solutions and the iron contents were determined by the proposed method.

After addition of 10·0 μg of iron 10·2 μg was found, 20·4 μg was found after addition of 20·0 μg and 49·5 μg was found after addition 50·0 μg. The precipitates produced from the solutions containing added iron were dried and treated with a mixture of ascorbic acid, sodium acetate and bathophenanthroline solutions (pH 4·7). No pink colour was discernible in these precipitates when compared with the similarly treated precipitate prepared from the solution containing no added iron. By adding small amounts of dilute standard iron solution (1 ml ≡ 1 μg of iron) to the latter precipitate and testing with the reagent mixture, it was found that about 0·7 μg of iron gave a perceptible pink colour.

The iron contents of two samples of cupric sulphate were determined in triplicate to assess the reproducibility of results obtained by this method. The results were 58, 58 and 62 p.p.m. of iron for one of the samples and 54, 58 and 56 p.p.m. for the other.

Known amounts of iron were then added to solutions of cupric sulphate and the iron contents of these solutions were determined to check recoveries. The results of these tests are shown in Table II.

TABLE II

RECOVERIES OF IRON ADDED TO CUPRIC SULPHATE SOLUTIONS

1 g of $CuSO_4.5H_2O$ was used in each test

Iron added, p.p.m.	Iron found, p.p.m.	Recovery, p.p.m.
0	58	—
100	155	97
200	255	197
200	255	197
300	348	290
400	456	398

The iron contents of several cupric salts were then determined by the proposed method. Determinations of the iron contents were also made with bathophenanthroline after electrolytic removal of the copper. A comparison of the results obtained by the two methods is given in Table III.

TABLE III

COMPARISON OF RESULTS FOR IRON, OBTAINED BY USING PROPOSED METHOD AND AFTER ELECTROLYTIC REMOVAL OF COPPER

1 g of cupric salt was used in each test

Salt	Iron content, p.p.m.	
	by proposed method,	after electrolysis,
Cupric acetate	Nil	Nil
Cupric chloride	64	64
Cupric nitrate	Nil	Nil
Cupric sulphate—		
Sample A	58	58
Sample B	56	54
Sample C	496	500
Sample D	76	70

These tests and the results quoted above show that precipitation of cuprous thiocyanate from homogeneous solution provides an effective method of separating large amounts of copper from small amounts of iron. Losses of iron by co-precipitation are negligible.

DETERMINATION OF LEAD

REAGENTS—

"Low in lead"-grade reagents should be used wherever possible.

Sodium metabisulphite solution—Dissolve 1·25 g of sodium metabisulphite in 100 ml of water. Filter if necessary.

Ammonium citrate solution—Dissolve 25 g of tri-ammonium citrate in 100 ml of water in a separating funnel. Extract with small portions of 0·02 per cent. dithizone until the extracts remain green. Discard the extracts. Make the solution just acid to litmus by adding 5 N hydrochloric acid and extract with successive small amounts of chloroform until the extracts are colourless.

Potassium cyanide solution, 10 per cent.—Dissolve 10 g of potassium cyanide in 100 ml of water in a separating funnel. Add 2 or 3 drops of 0·02 per cent. dithizone solution and a few millilitres of chloroform. Extract, and discard the organic layer. Repeat the extraction with dithizone and chloroform until the extract is no longer red, but has a greenish hue or is colourless. Continue extracting with chloroform only until the extracts are colourless.

Potassium cyanide solution, 0·5 *per cent.*—Dilute 5 ml of 10 per cent. potassium cyanide solution to 100 ml with water.

Dithizone solution, 0·02 *per cent.*—Dissolve 0·02 g of dithizone in 100 ml of chloroform. This solution should be stored in a darkened glass bottle in a refrigerator.

Dithizone solution, 0·002 *per cent.*—Dilute 10 ml of 0·02 per cent. dithizone to 100 ml with chloroform. This solution should be freshly prepared.

Nitric acid, 1 *per cent.*—Dilute 1 ml of colourless nitric acid, sp.gr. 1·42, to 100 ml with water.

Standard lead solution—Dissolve 1·60 g of lead nitrate in 50 ml of nitric acid, sp.gr. 1·42, and add sufficient water to produce 1 litre.

$$1 \text{ ml} \equiv 1 \text{ mg of lead.}$$

Dilute standard lead solution—Dilute 10 ml of the standard lead solution to 1 litre with water. Dilute 20 ml of this solution to 100 ml with water. This solution should be freshly prepared.

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

PREPARATION OF CALIBRATION GRAPH—

Measure amounts of dilute standard lead solution to cover the range 0 to 12 μg of lead into separate 100-ml separating funnels. Dilute each portion with 40 ml of water, add 2 ml of sodium metabisulphite solution, 2 ml of ammonium citrate solution and 3 ml of 10 per cent. potassium cyanide solution. Adjust the pH of the solution to between 9 and 10, if necessary, by adding ammonia solution.

Extract the solution three times with 5-ml portions of 0·02 per cent. dithizone solution, shaking for 2 minutes for each extraction, and combine the extracts in another separating funnel. Discard the aqueous phase.

To the combined extracts add 10 ml of 1 per cent. nitric acid, shake for 2 minutes, allow to separate and carefully discard the organic layer. Add a few drops of chloroform, without mixing, to collect any remaining dithizone solution and again carefully discard the organic layer.

Add 0·2 ml of ammonium citrate solution and raise the pH of the solution to between 9 and 10 by adding ammonia solution (about 0·6 ml of 5 N ammonia is required), add 0·2 ml of sodium metabisulphite solution and 0·2 ml of 10 per cent. potassium cyanide solution.

Add 0·5 ml of 0·002 per cent. dithizone from a 10-ml burette. Extract by shaking for 2 minutes, allow to separate, and transfer the organic phase to another separating funnel. Continue the extraction with 0·5-ml portions of the dithizone solution, combining the extracts, until two successive extracts remain green. Note the burette reading.

From another 10-ml burette, add sufficient chloroform to the combined extracts to produce a volume of 10·0 ml. Add 15 ml of 0·5 per cent. potassium cyanide and shake for 30 seconds to remove excess dithizone from the organic layer. Dry the stem of the funnel and run the organic layer into a 1-cm spectrophotometer cell.

Measure the optical density of the solution at 518 mμ, using as reference the solution containing no added lead. The graph relating optical density to amount of lead present should be linear and pass through the origin.

METHOD—

Transfer a portion of the filtrate resulting from precipitation of the cuprous thiocyanate (p. 42), and containing not more than 12 μg of lead, to a separating funnel. Add 2 ml of sodium metabisulphite solution and 2 ml of ammonium citrate solution and adjust the pH of the solution to about 9 by adding ammonia solution. Add 3 ml of 10 per cent. potassium cyanide solution.

Extract the solution three times with 5-ml portions of 0·02 per cent. dithizone solution, shaking for 2 minutes for each extraction. Combine the extracts in another separating funnel and complete the determination as described under "Preparation of Calibration Graph." Prepare the reference solution from the blank solutions used on the precipitation reagents.

RESULTS—

Known amounts of lead were added to a series of solutions prepared from electrode copper-rod (Johnson Matthey & Co. Ltd.) containing less than 1 p.p.m. of lead. The lead

contents of the solutions were determined by the proposed method and the results are given in Table IV. The recoveries of added lead were satisfactory.

TABLE IV

RECOVERIES OF LEAD FROM SOLUTIONS PREPARED WITH PURE COPPER

Weight of copper in solution, mg	Lead added, µg	Lead found, µg
80	10·0	10·1
150	10·0	10·2
250	5·0	5·0
250	10·0	9·9
250	20·0	19·9

The lead contents of four copper salts were determined by the proposed method and by the method of Silverman.[10] In all the lead assays, 1 g quantities of each salt were used and, after precipitation and filtration, half of each filtrate was used in the colorimetric method. The results are given in Table V. The results obtained by the two methods are in fairly good agreement.

TABLE V

COMPARISON OF LEAD CONTENTS DETERMINED BY THE PROPOSED METHOD AND BY SILVERMAN'S METHOD

Salt	Lead content, p.p.m., found by using	
	proposed method	Silverman's method
Cupric acetate	5·6	7·4
Cupric chloride	22·4	20·8
Cupric nitrate	0·8	0·5
Cupric sulphate	10·0	8·6

Recovery experiments were also carried out by adding known amounts of lead to solutions of cupric acetate and cupric sulphate and determining the lead by the proposed method. These results are summarised in Table VI. The recoveries obtained were quite good.

TABLE VI

RECOVERY OF ADDED LEAD

Salt	Lead content, p.p.m.,		
	added,	found,	recovered,
Cupric acetate	0	5·6	—
	10·0	16·2	10·6
	20·0	25·4	19·8
Cupric sulphate	0	10·0	—
	10·0	20·4	10·4
	20·0	30·0	20·0

The possibility of loss of lead by co-precipitation with the cuprous thiocyanate was investigated in two ways. Firstly, by addition of lead to pure copper, and secondly, by determining the lead content of four solutions of cupric chloride containing different

TABLE VII

DETERMINATION OF THE LEAD CONTENT OF DIFFERENT WEIGHTS OF CUPRIC CHLORIDE SAMPLE

Weight of cupric chloride, grams	Lead found, µg	Lead content, p.p.m.
0·25	5·6	22·4
0·5	11·2	22·4
0·75	16·8	22·4
1·0	22·4	22·4

weights of the sample. The results, which are given in Table VII, were identical. It follows, therefore, that if any lead had co-precipitated, the amount lost in this way was proportional to the weight of cuprous thiocyanate.

Conclusions

Precipitation of cuprous thiocyanate from homogeneous solution provides a convenient separation of copper from traces of iron and lead. No lead or iron is lost during the precipitation, whereas the conventional precipitation of cuprous thiocyanate leads to erratic results. The determinations of iron and lead, both of which remain in the filtrate, may be made by using bathophenanthroline and dithizone, respectively.

The method has been adopted for routine use in our laboratories for the gravimetric assay of cupric salts, and portions of the filtrate are used for determining iron and lead. For routine colorimetric purposes, however, we now use 1,10-phenanthroline to determine iron, since it provides a much quicker, though less sensitive, method of colorimetric measurement.

The use of precipitation from homogeneous solution as a separation method in trace metal analysis is a new and interesting application of this technique.

We thank Mr. D. W. Wilson, Head of the Chemistry Department of the Sir John Cass College, for his interest and guidance, and the Directors of Hopkin & Williams Ltd. for permission to publish this work.

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The Application of an Electrolytic Hygrometer to the Determination of Oxide in Lead

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A method is described for determining oxide in lead by hydrogen reduction with the subsequent use of an electrolytic hygrometer to determine the evolved water. Details are given of an improved and simplified hygrometer whose electrodes can be removed for cleaning and re-coating. A modification to a standard potentiometer recorder is also described that permits the recorder to control the rate of application of water to the detector.

Results are quoted showing an accuracy for the method of within about 8 per cent. for oxide contents of 10 p.p.m., and oxide contents of greater than 0·1 per cent. can be determined with an accuracy of within about 2 per cent. It is indicated that the determination of other metallic oxides may be carried out in a similar manner.

In the course of research into the metallurgical properties of dispersion-hardened lead, the determination of oxide in a large number of samples having a wide range of oxide contents was required.

The most convenient method for this analysis is by reduction with hydrogen[1] or hydrogen sulphide[2] and subsequent determination of the evolved water. If the amount of evolved water is greater than a few milligrams, gravimetric determination is normally adequate. However, for smaller amounts other methods of measuring the water are desirable. Keidel[3] described an electrolytic moisture meter in which the water is absorbed by a layer of phosphorus pentoxide supported by platinum electrodes across which is applied an e.m.f. The resulting electrolysis current is directly related by Faraday's law to the amount of water absorbed.

We have developed a method in which the water produced by the reduction of lead oxide by hydrogen is determined electrolytically by a similar device.

Apparatus

Crawshaw and Davidson[4] described in some detail the construction of an electrolytic hygrometer of the type developed by Keidel. Initial experiments with a detector constructed in a similar manner showed the feasibility and simplicity of the measurement of water from reduced metal oxides by this method, but some modification of the detector seemed desirable. The form of the detector has been radically changed to permit the electrodes to be removed for cleaning and re-coating, if necessary, and the electrical connections have been made more reliable. A detector of design similar to that finally adopted by us has been described by Barendrecht.[5]

The complete apparatus is shown diagrammatically in Fig. 1, and a description of the separate components is given below.

Purification train—

In order to reduce blank values to a minimum, oxygen and water are removed from both hydrogen and nitrogen supplies.

Nitrogen—A Pyrex-glass tube with an external resistance wire winding is filled with cupric oxide supported on kieselguhr, as described by Dodd and Robinson.[6] The cupric oxide is reduced by hydrogen at a temperature of 170° C before use, the same temperature being used for the nitrogen purification.

The oxygen-free gas is dried by passage through two glass columns, 12 inches long and 1 inch in diameter; the top half of the first column is filled with silica gel and the bottom half with anhydrone, and the second column is filled with phosphorus pentoxide supported on polythene granules. The outlet from the second column is connected through a T-piece to the three-way taps, A and B, which are themselves connected to the inlet of the combustion tube and to the outlet of the detector, respectively.

Hydrogen—Oxygen is removed by passing the gas through two Deoxo catalytic purifiers followed by a drying train similar to that described above for nitrogen, the outlet being connected directly to the second arm of the three-way tap A. Adequate control of the flow-rates of both gases is obtained by using two-stage reducing valves on the gas cylinders followed by needle valves.

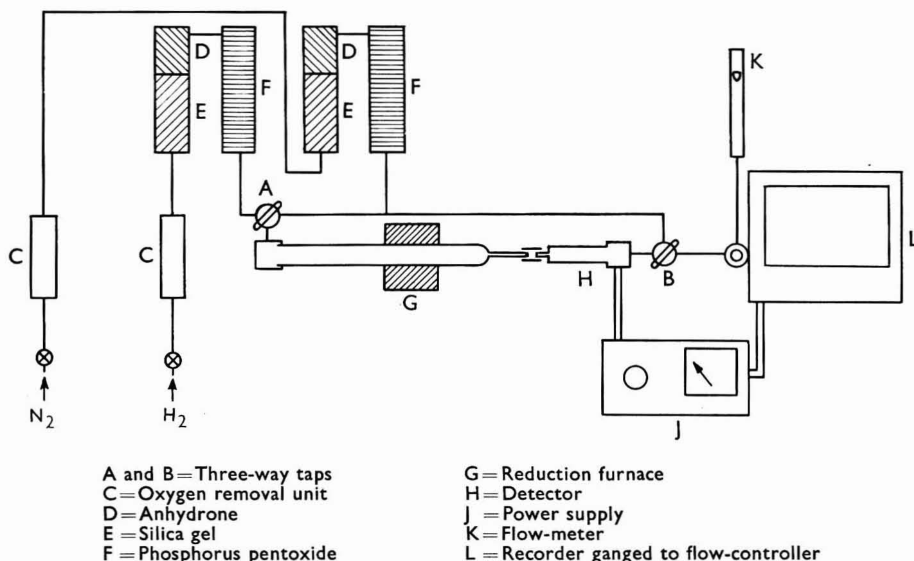


Fig. 1. Apparatus for determining oxide in lead

It was found essential in both gas trains to ensure complete freedom from leaks and to use the minimum number of rubber connections.

COMBUSTION FURNACE—

A small resistance furnace is used having a hot zone of about 8 cm long and a maximum working temperature of about 800° C. This is fitted with a silica combustion tube, 36 cm in length and 2 cm in diameter, the outlet end of which is reduced to 8 mm diameter. The detector is connected to the combustion tube with a short length of rubber tubing, butting the silica and glass tubes together.

The inlet end of the combustion tube is fitted with a duralumin end-cap having a sample port with O-ring seal and a gas inlet connected to the three-way tap A.

The second three-way tap, B, on the outlet end of the detector allows nitrogen to be passed through the detector and combustion tube in the reverse direction during sample loading to minimise the ingress of moist air.

By using the combustion tube described, up to four small silica boats can be loaded, together with a nickel "pusher." The silica boats are semi-cylindrical, 20 mm long, 10 mm wide and 5 mm deep.

ELECTROLYTIC DETECTOR—

The detector is shown in Fig. 2. The electrode support is made from a $4\frac{1}{2}$-inch length of $\frac{1}{2}$-inch diameter polytetrafluoroethylene rod machined to be a good push fit in a length of selected glass tube. The diameter of the rod is reduced by 0·012 inch for a length of $2\frac{1}{2}$ inches, starting $\frac{1}{4}$ inch from one end; for a length of $1\frac{1}{2}$ inches from the other end the diameter is reduced to $\frac{3}{8}$ inch, leaving two shoulders $\frac{1}{4}$ inch in length. A double-start thread of 48 threads per inch is cut in the region between the shoulders. The threads are V-shaped and cut to a depth of 0·003 inch by using a sharp lathe tool. To permit gas flow, two grooves are cut in each

shoulder about 0·010 inches deep. The contact springs are formed from $\frac{1}{8}$-inch wide phosphor-bronze strip, 0·015-inch thick, and fixed to the end of the support by two 10 BA stainless-steel set-screws. The electrodes consist of two 0·005-inch diameter platinum wires. It was found most convenient to wind each electrode separately. One end of the wire is passed through a 0·020-inch diameter hole bored longitudinally in the polytetraethylene shoulder and soldered to one of the contact springs between the set screws. The wire is then wound tightly in one of the threads, passed through a 0·020-inch diameter hole in the other shoulder and fixed in position by a 10 BA stainless-steel set-screw and washer, screwed into the end of the support. The other electrode is fitted in the same way.

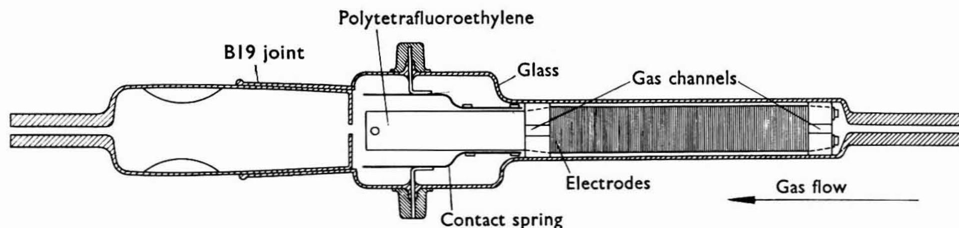


Fig. 2. Electrolytic detector

The outer Pyrex-glass tube has a bore of $\frac{1}{2}$ inch in the region of the electrodes and increases to about a 1-inch bore around the contact springs, where L-shaped tungsten contacts are fused through the glass. This end of the tube is fused to a B19 socket taking a cone having a short length of thick-wall glass tubing of about 8 mm diameter. A length of the same tubing is also fused to the inlet end of the detector tube.

After a thorough cleaning and de-greasing, the electrodes are coated with electrolyte by uniform application of a solution of phosphoric acid in acetone. An optimum film thickness of 0·00015 inch of phosphorus pentoxide is obtained by applying about 1 ml of a 1 per cent. solution. A convenient method of applying the electrolyte is to use a motor-driven syringe connected by polythene tubing to a fine jet which is traversed across the electrodes. The electrode support is rotated during the coating process, and a current of air is used to accelerate evaporation of the solvent. The coated electrodes are inserted carefully into the glass tube so that the contact springs are held firmly between the tungsten contacts. The assembled detector is connected to a dry air or nitrogen supply with a flow rate of about 100 ml per minute, and electrical connection made to the d.c. power supply. Initially the detector has an extremely low resistance, and care must be taken to ensure that the electrolysis current does not exceed 10 mA, otherwise excessive frothing of the electrolyte will occur. This is prevented either by lowering the output voltage of the power pack or, more simply, by fitting a limiting resistor in series with the detector.

After approximately 1 hour the detector current should have fallen to less than 130 μA ($<$ 10 p.p.m.). Further drying time depends on the desorption of moisture from the system to which the detector is connected, but in most simple glass systems a standing current of less than 25 μA ($<$ 2 p.p.m.) is obtained in a few hours.

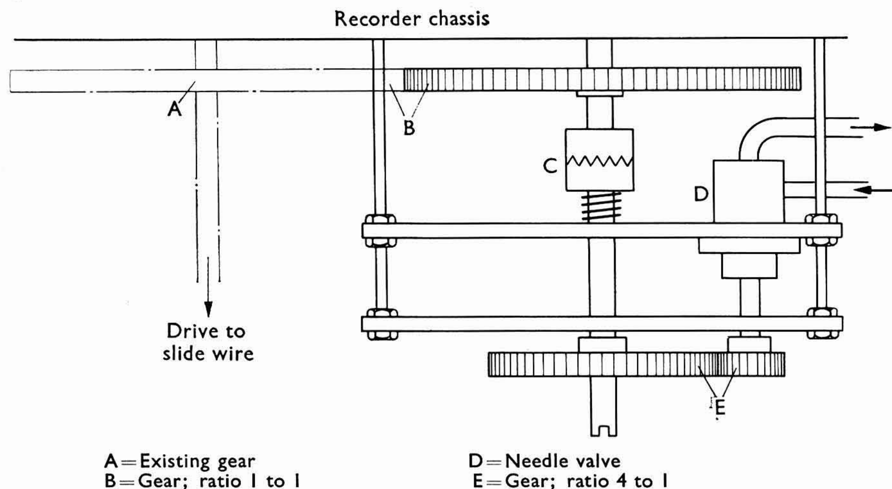
ELECTRICAL CIRCUIT—

The circuit consists of a d.c. source and a sensitive ammeter in series with the detector. Keidel[3] has described a practical circuit, for use with the detector, to measure moisture in gas streams; with this circuit an electrolysis current of 13·2 μA corresponds to 1 p.p.m. of water, by volume at 25° C, and a flow-rate of 100 ml per minute. His circuit incorporates meter shunts to give full-scale deflections on a 100-μA meter for 1000, 300, 100, 30 and 10 p.p.m. (*i.e.*, shunt control is marked "scale factor $\times$ 10," $\times$3," $\times$1," etc.). This circuit has been found suitable for application in the work described in this paper, except that we have found that an improved detector response is obtained if the e.m.f. is raised to about 70 volts.

In the measurement of discrete amounts of water, as in this method, the integrated current is required. Therefore, the circuit incorporates a 250-ohm potentiometer in the meter shunt, permitting current recording with a 5-mV potentiometric recorder and subsequent integration of the current - time curve.

FLOW-CONTROLLER—

In order to keep the electrolysis current within the range of the measuring instrument, the rate of application of water to the detector must be controlled. This is most easily done by mechanically driving a needle valve from the potentiometric recorder, thus limiting the current for each range of the moisture meter by controlling the flow-rate of the gas through the detector.



A = Existing gear
B = Gear; ratio 1 to 1
C = Dog clutch
D = Needle valve
E = Gear; ratio 4 to 1

Fig. 3. Flow-controller, showing modification to potentiometric recorder

An Edwards' needle valve is suitable when geared to the recorder slide-wire drive as shown in Fig. 3 so that an increasing recorder deflection closes the valve. A lever-operated dog clutch permits adjustment of the fully-closed position of the valve with respect to the recorder reading in order to prevent over-shooting of the full-scale position during rapid current increases. This modification can be made to an A.E.I. recorder (type 10 S), but suitable adaption of other similar recorders should be possible. The carrier gas is conveyed from the detector outlet (tap B) to the controller by rubber tubing and then to a float-type flow-meter. This gives visual indication that the controller is operating satisfactorily and is needed for the initial setting-up of the needle valve position.

PROCEDURE

Before the start of a determination remove traces of oxygen or water that may have accumulated in the system, by passing first nitrogen and then hydrogen through the combustion furnace (at 500° C) until a steady base current is obtained. Adjust the flow-rate of both gases to 100 ml per minute with the flow controller fully open. Pass nitrogen for 5 minutes to remove hydrogen, and then, with nitrogen passing in the reverse direction, load up to four small silica boats containing a suitable weight of sample and a nickel "pusher" into the cold zone of the furnace tube. Close the end-cap, and pass nitrogen in the forward direction for 5 minutes to remove residual air. Transfer the first sample boat to the hot zone, and continue passing nitrogen until a steady base current is reached.

By means of the three-way tap replace the nitrogen flow with hydrogen, continuing the reduction until the current drops to the hydrogen base-line previously determined. Calculate the percentage of oxide by measuring the area beneath the recorded current - time curve.

Flush the furnace with nitrogen for 5 minutes, transfer the second sample to the hot zone, and continue as before.

To obtain the most accurate results with samples producing less than about 200 μg of water it is necessary to obtain a blank value corresponding to the oxidation of the sample during the pre-heating period by traces of oxygen remaining in the nitrogen. This is carried out as described below.

Pass nitrogen over the hot fully reduced sample, after oxide determination, for a period similar to that required for the pre-heating period. Carry out a second reduction with

hydrogen, and measure the small area corresponding to the blank value. No blank determination is required when standard samples of lead oxide are being analysed.

NOTES—

The accurate determination of oxide by integration of the areas produced in the above procedure is dependent to a considerable degree on the attainment of a steady base current of the lowest possible magnitude.

Although standing currents equivalent to a few parts per million of water are easily obtained when passing nitrogen through the detector, it is found that with hydrogen the standing current is equivalent to approximately 10 p.p.m. of water. It has been suggested that these increased currents are due to a re-combination effect, and a mechanism involving the catalytic action of a platinum oxide film on the electrodes has been proposed by Czuha, Gardiner and Sawyer.[7]

When determining milligram amounts of water, an accurate value is obtained simply by measuring the area above the hydrogen base line drawn parallel to the chart zero. For routine analysis, considerable time saving can be achieved by extrapolation over the final stages of the curve once the base line has been determined.

The measurement of areas derived from microgram amounts of water necessitates a more critical study of the current - time curves.

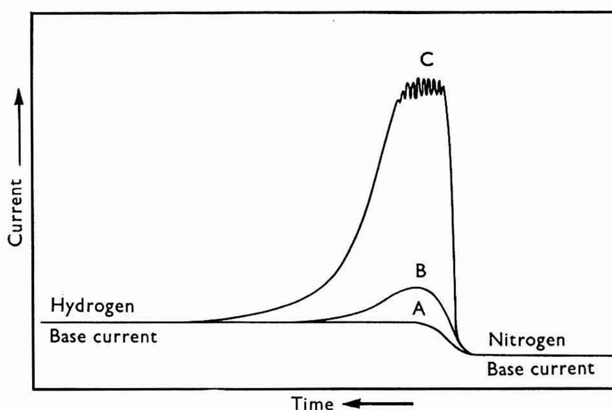


Fig. 4. Typical reduction curves: curve A, change in base-line when changing from nitrogen to hydrogen flow; curve B, blank determination; curve C, sample determination

In Fig. 4, curve A represents the change in base-line when changing from nitrogen to hydrogen flow. Curves B and C are typical of blank and sample determinations, respectively. The weights of water produced are calculated from the areas enclosed by curves A and B for the blank value, and A and C for the sample. It follows therefore that, by superimposing curve B on to curve C, the area representing the weight of water produced from the sample can be measured directly.

The full-scale recorder deflection

$$= \text{Scale factor} \times 1{\cdot}320 \text{ mA}.$$

Therefore, from Faraday's law and if the chart speed is 12 inches per hour and a 10-inch recorder scale is used, then—

$$\text{Chart area of 1 sq. inch} = 3{\cdot}70\ \mu\text{g of water} \times \text{scale factor}$$
$$= 3{\cdot}28\ \mu\text{g of oxygen} \times \text{scale factor}.$$

RESULTS AND DISCUSSION

During the past year this method has been successfully applied to many samples of extruded lead and lead powder. In order to assess the repeatability, one particular sample was used to carry out several determinations. Most extruded samples, although having a fairly low content of oxide, showed considerable heterogeneity, and therefore a well mixed

powder sample was selected. To asses the repeatability at low levels of oxide, small samples of the powder were used (about 10 mg) for one series of determinations. Under normal circumstances about 0·5-g samples would be used. The results obtained are shown in Table I.

To assess the accuracy various sample weights of analytical-reagent and Specpure lead oxide, PbO, were also analysed; these results are also shown in Table I.

During the development of the detector it was considered necessary, in view of the radical changes in design, to have an independent assessment of the efficiency of absorption and electrolysis. This was carried out by the electrolysis of dilute sulphuric acid, oxidation of the generated hydrogen in a nitrogen gas stream by heated copper oxide and measurement of the water produced. The comparison of the generating and detector currents gave a direct measure of the detector efficiency. This was found to be greater than 99 per cent. at flow-rates up to 200 ml per minute.

TABLE I

TYPICAL RESULTS

Sample	Sample weight, mg	Corrected area, sq. inches	Blank value, $\mu g\ H_2O$	Corrected weight, $\mu g\ H_2O$	Oxygen content, %	Mean, %	Coefficient of variation
Lead powder	650	24·3	—	899	0·123	0·124	1·09
	650	24·5	—	906	0·124		
	656	24·8	—	917	0·124		
	657	24·8	—	917	0·124		
	652	24·8	—	917	0·125		
	1003	36·9	—	1363	0·121		
Lead powder*	8·00	2·9	2·2	11	0·119	0·126	7·13
	4·63	1·9	1·8	7·0	0·134		
	10·55	3·9	1·1	14	0·121		
	11·1	4·7	1·1	17	0·139		
	4·22	1·7	3·3	6·3	0·132		
	18·6	6·3	2·6	23	0·111		
	5·80	2·2	6·7	8·1	0·124		
Lead oxide, PbO†	9·2	19·7	—	728	7·02	7·08	1·69
	10·9	24·1	—	891	7·26		
	9·6	20·4	—	755	6·97		
	14·2	30·1	—	1113	6·95		
	9·5	20·4	—	755	7·05		
	10·2	22·5	—	832	7·22		

* A scale factor of × 1 was used; for the rest of the results a scale factor of × 10 was used.

† Theoretical oxygen content, 7·17 per cent.

CONCLUSIONS

The proposed procedure has proved to be a rapid, accurate and sensitive method for determining oxide in lead over a wide range of oxide contents. For oxide contents of 0·1 per cent. the accuracy is to within about 2 per cent., and at the 10 p.p.m. level the accuracy is within about 8 per cent. With experience, up to ten samples a day may be analysed, and a permanent record is obtained.

With modification of furnace temperature the oxide content of other metals can be determined, if the oxide is reduced by hydrogen. We have used the method for determining oxide in copper, with a furnace temperature of 950° C, and some success has been obtained by using hydrogen sulphide for the reduction of zinc oxide.

The detector itself can also be used for other analyses involving the determination of traces of water.

We thank the Directors of Associated Electrical Industries (Woolwich) Ltd. for permission to publish this paper.

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The Determination of the Free Sulphur Dioxide Content of Ciders

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The conditions necessary for determining free sulphur dioxide in cider were established by studying the rate of removal of sulphur dioxide from aqueous solutions by a gas stream. The cider is acidified and the free sulphur dioxide removed at room temperature in an air-stream under reduced pressure; it is then absorbed in neutralised hydrogen peroxide and titrated with standard alkali. Possible interferences are considered and allowed for by applying a correction for the blank value.

WHEN sulphur dioxide is used as a preservative in ciders, wines and other fruit beverages, part of it combines with the carbonyl compounds present to form hydroxysulphonates ("bisulphite compounds") and part remains free in the inorganic state, mainly as sulphurous acid and bisulphite ions. It is widely recognised that only free sulphur dioxide is effective against micro-organisms, and it is therefore important to be able to determine this analytically.

Ripper's method,[1] of iodimetric titration in acid solution without previous treatment with alkali, is the one most commonly used for determining free sulphur dioxide in ciders and similar beverages. Unfortunately, it also records other substances oxidisable by iodine, and for this reason the end-point is often ill defined. The errors involved in this method and various attempts to overcome them were reviewed by Joslyn and Bravermann.[2]

The colorimetric method of Steigman,[3] involving the use of pararosaniline and formaldehyde, has been developed by Stone and Laschiver[4] for determining both free and total sulphur dioxide in beer. With ciders, however, interference by polyphenols greatly reduces its sensitivity for determining free sulphur dioxide and renders it useless for determining total sulphur dioxide.

Kielhöfer and Aumann[5] and Paul[6] removed free sulphur dioxide from acidified wine at room temperature by a stream of air, absorbed it in neutralised hydrogen peroxide and titrated with 0·01 N sodium hydroxide. This method is based on sound theoretical principles and appeared worthy of investigation. When the wine (10 or 20 ml) is acidified with 5 ml of 25 per cent. v/v orthophosphoric acid, the pH is lowered to between 1 and 1·5. This has the double purpose of rendering the free sulphur dioxide more volatile and of greatly reducing the rate of decomposition of the combined sulphur dioxide; furthermore, at this pH sulphur dioxide resists oxidation by the atmosphere. Kielhöfer and Aumann passed a stream of air for 30 minutes, whereas Paul, possibly using a more rapid rate of flow, found that 15 minutes was sufficient. However, as observed by Kielhöfer and Aumann, the precise stoicheiometric removal of free sulphur dioxide from a wine is not to be expected, since even at this low pH there is a slight tendency for combined sulphur dioxide to dissociate once the equilibrium is disturbed by removal of the free sulphur dioxide. Kielhöfer and Aumann found that the amount of sulphur dioxide liberated in this way was small, even if the wine was aerated for a long time, and they regard the value obtained after 30 minutes as being the best practicable estimate of free sulphur dioxide. The extent of the dissociation of bound sulphur dioxide will, however, depend on the nature and amount of the carbonyl substances present in the particular sample and cannot always be assumed to be negligible.

The method described in this paper is a modification of the methods of Paul and of Kielhöfer and Aumann; it was developed from a study of the conditions necessary to ensure complete removal of sulphur dioxide from solution in the absence of combined sulphur dioxide.

RATE OF REMOVAL OF SULPHUR DIOXIDE FROM DILUTE ACID SOLUTION

The problem of removing sulphur dioxide from solution at a given temperature and pH is a physical one, and depends on the flow-rate of carrier gas and on the partial pressure of the sulphur dioxide. The flow-rate of gas should be as fast as possible, consistent with efficient trapping of the entrained sulphur dioxide by the absorbing solution.

In a preliminary experiment nitrogen was bubbled through a solution of sodium hydrogen sulphite (0·85 M) in 5 per cent. v/v orthophosphoric acid. Portions (20 ml) were removed and titrated with 0·01 N iodine. The concentrations of sulphur dioxide remaining in solution after different times were—

Length of bubbling time, minutes ..	0	10	15	20	30	40
Sulphur dioxide remaining, p.p.m. ..	54	24	7	4	1	trace

It appears, therefore, that bubbling for at least 30 minutes is required for the complete removal of sulphur dioxide from solution under these conditions. This was attributed to the extremely low partial pressure of sulphur dioxide in the carrier gas when the concentration of sulphur dioxide in solution had been reduced to about 10 p.p.m. This difficulty could obviously be overcome by removing the sulphur dioxide under a partial vacuum.

A similar experiment was carried out, in which a stream of nitrogen at a pressure of 80 mm of mercury was drawn through the solution, by using a water-pump; the concentrations of sulphur dioxide remaining in solution after different times were—

Length of bubbling time, minutes ..	0	5	10	15
Sulphur dioxide remaining, p.p.m. ..	53	12	1	nil

Similar results were obtained in a further experiment in which a stream of air at 80 mm pressure was used. Removal of sulphur dioxide was therefore complete in 15 minutes, and this provided the basis for the method described below. The hydrogen peroxide solution used for absorbing the sulphur dioxide was shown to be completely stable to aeration under reduced pressure for 15 minutes.

METHOD

APPARATUS—

The apparatus (see Fig. 1) is similar to that described for determining total sulphur dioxide,[7] but requires only two absorption tubes, A and B, and no condenser. The 250-ml round-bottomed flask, having a B24 neck joint and a side inlet, and the B14 air-leak and the tubes (200 × 25 mm) are standard pieces of glassware. The absorption heads are made from B24 cone joints with the internal delivery tubes drawn out to a jet. The second absorption tube, B, is connected to a mercury manometer and a water-pump.

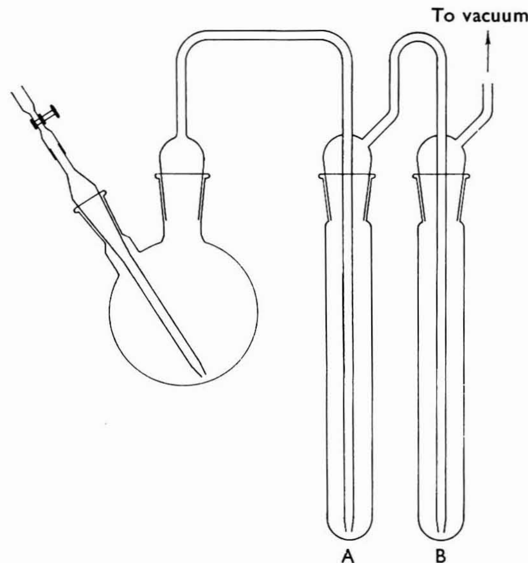

Fig. 1. Absorption apparatus

REAGENTS—

Hydrogen peroxide, 1 per cent. w/v—Dilute 3·3 ml of 100-volume analytical-reagent grade hydrogen peroxide to about 90 ml with distilled water. Add 1 ml of Tashiro indicator (2 volumes of 0·1 per cent. methyl red, *plus* 1 volume of 0·1 per cent. methylene blue, both in 95 per cent. ethanol), and neutralise with 0·01 N sodium hydroxide to the first appearance of a green colour. Dilute to 100 ml.

Sodium hydroxide, 0·01 N—Prepare in the usual way, store in an automatic 10-ml burette with soda-line guard tubes and standardise against potassium hydrogen iodate. It is convenient to use the same solution of potassium hydrogen iodate, suitably diluted, to standardise 0·01 N sodium thiosulphate for determining total sulphur dioxide.[7]

Orthophosphoric acid, 25 per cent. v/v—Containing 250 ml of 85 per cent. w/v orthophosphoric acid per litre.

PROCEDURE—

By pipette, transfer 5 ml of 1 per cent. hydrogen peroxide into each absorption tube. Similarly transfer 10 or 20 ml of sample to the flask, and add 5 ml of 25 per cent. orthophosphoric acid.

Attach the flask to the apparatus, and evacuate to a pressure of 70 to 80 mm while admitting a steady stream of air, controlled by the clip on the inlet tube. After 15 minutes shut off the vacuum, and carefully open the screw-clip. Lower the first absorption tube, A, and expel the drop of solution in the tip of the delivery tube by warming the flask with the hand; rinse the delivery tube. Titrate the contents of tube A with 0·01 N sodium hydroxide to a grey end-point. Replace the tube on the apparatus to rinse the inside of the delivery tube; re-adjust the end-point, if necessary.

Immediately attach to the apparatus another absorption tube, A′, containing 5 ml of 1 per cent. hydrogen peroxide. Close the screw clip, apply the vacuum, and continue aeration for a second 15 minutes (including the time taken in titrating the contents of tube A, normally about 2 minutes). Finally remove tube A′, titrate the contents as described above, and subtract from the result of the titration of tube A, the blank value obtained. The reasons for this blank value are discussed below.

Calculate results as p.p.m. of sulphur dioxide.

$$1 \text{ ml of } 0{\cdot}01 \text{ N sodium hydroxide} \equiv 0{\cdot}32 \text{ mg of sulphur dioxide.}$$

The absorption of sulphur dioxide in tube A is highly efficient, and the second tube, B, rarely yields any significant titration unless the hydrogen peroxide in tube A is completely reduced by sulphur dioxide. This occurs only with samples containing an extremely high concentration of free sulphur dioxide (much beyond the limits of normal cider), since 5 ml of 1 per cent. hydrogen peroxide will oxidise 100 mg of sulphur dioxide.

DISCUSSION OF METHOD

RECOVERY OF FREE SULPHUR DIOXIDE—

The method was tested by comparing the recovery of free sulphur dioxide (10-ml portions containing 200 p.p.m.) from a solution containing 0·157 g of sodium metabisulphite ($Na_2S_2O_5$) per 500 ml with that obtained simultaneously by titrating the same solution into 10-ml portions of 0·01 N iodine. To ensure that the two methods should be strictly comparable, 0·1 N hydrochloric acid was used as a common standard for both the 0·01 N sodium hydroxide and the 0·01 N iodine (via potassium iodate and 0·1 N sodium thiosulphate).

Results of three determinations showed 100·0, 100·2 and 100·2 per cent. recovery; in each determination the second absorption tube remained neutral, and no residual sulphur dioxide was detectable (by 0·01 N iodine and starch) in the contents of the flask.

It is, unfortunately, not possible to test the recovery of free sulphur dioxide in the presence of cider, because, when standard sodium hydrogen sulphite is added to cider, part of it combines with the carbonyl substances present. Nor is there any established method for the precise determination of free sulphur dioxide in cider, with which the present method could be compared. It is, however, reasonable to assume that, since the proposed method gives complete recovery of sulphur dioxide from sodium hydrogen sulphite solution, it will also give complete recovery from cider.

Two factors may, however, lead to high results; these are the presence of volatile acids in the cider and the liberation of free sulphur dioxide by dissociation of "bisulphite compounds" during the determination.

EFFECT OF VOLATILE ACIDS—

The volatile acidity of cider is normally not more than about 0·1 per cent. as acetic acid. If any of this is carried over in the air stream it may be trapped in the absorption tube and so be recorded as sulphur dioxide. The probable size of the blank value due to volatile acid was investigated by determining the apparent free sulphur dioxide content of 0·2 per cent. acetic acid. Results correspond to 2·5 p.p.m. as sulphur dioxide on a 20-ml sample and were substantially unchanged in the blank solution, tube A', collected during the second 15 minutes. In a normal cider, therefore, with a much lower volatile acidity, the error caused by volatile acids should be less than 2·5 p.p.m. and can be allowed for by subtracting the blank value.

DISSOCIATION OF COMBINED SULPHUR DIOXIDE—

The equilibrium between free and combined sulphur dioxide in a cider at a given temperature and pH depends on the concentrations of the carbonyl compounds present and on the equilibrium constants of their "bisulphite compounds". If the free sulphur dioxide is removed, as in the proposed procedure, each "bisulphite compound" dissociates into free sulphur dioxide and free carbonyl compound at a rate dependent on its concentration and on the velocity constant of its decomposition. These velocity constants are greatly reduced by lowering the pH, but even at pH 1·5 the dissociation is measurable and may interfere in the determination of free sulphur dioxide. It is therefore to be expected that part of the sulphur dioxide determined in the blank titration, tube A', is caused by the dissociation of combined sulphur dioxide; this may be called the "dissociation blank value."

In ciders and similar alcoholic beverages much of the combined sulphur dioxide is present as acetaldehyde bisulphite, but other carbonyl compounds are also involved. Burroughs and Whiting[8] have calculated the sulphite-binding power of certain of the known constituents of cider, and Kielhöfer and Wurdig[9,10] have examined similar problems in wines.

The liberation of sulphur dioxide combined with acetaldehyde, pyruvic acid and glucose was investigated in model systems. A solution, containing 100 p.p.m. of sulphur dioxide as acetaldehyde bisulphite in dilute phosphate - citrate buffer at pH 3·5, yielded a blank value, tube A', of only 0·3 p.p.m. in the determination of free sulphur dioxide; dissociation of acetaldehyde bisulphite is therefore negligible under these conditions. This was confirmed by an experiment in which a solution containing 200 p.p.m. of sulphur dioxide and 70 p.p.m. of acetaldehyde was allowed to come to equilibrium, thus giving approximately 100 p.p.m. of free and 100 p.p.m. of combined sulphur dioxide. The results for the determination of free sulphur dioxide by the proposed method (excluding the correction for the blank value) agreed within 1 p.p.m. with those by direct iodimetric titration of the original solution at pH 1·5. There was similarly close agreement between the bound sulphur dioxide content (determined by iodimetric titration at pH 8·1[11]) of the original solution and of the contents of the flask after determination of free sulphur dioxide. The presence of acetaldehyde bisulphite in the sample, therefore, does not interfere in the determination of free sulphur dioxide by the proposed method, nor does it contribute appreciably to the dissociation blank value.

An experiment, similar to the iodimetric determination described above, was carried out on a solution containing 200 p.p.m. of total sulphur dioxide and 220 p.p.m. of sodium pyruvate, again corresponding to approximately 100 p.p.m. of free and 100 p.p.m. of combined sulphur dioxide. Here, the apparent free sulphur dioxide determined by vacuum aeration was 8 to 9 p.p.m. higher than by direct iodimetric titration, with a corresponding loss of bound sulphur dioxide in the contents of the flask. The amount of free sulphur dioxide liberated during the second 15 minutes aeration, tube A', was 6 to 7 p.p.m., so that a close approximation to the true value could be obtained by subtracting this correction.

It can be calculated from the results obtained by Vas[12] for glucose, that the amount of glucose bisulphite likely to occur in a normal cider is small, corresponding to only 8 p.p.m. of combined sulphur dioxide at 1·8 per cent. of glucose and 50 p.p.m. of free sulphur dioxide. It can also be calculated that, at pH 1·5, only 0·5 per cent. of the glucose bisulphite present will dissociate in 15 minutes at 20° C. The effect of this on the determination of free sulphur

dioxide in ciders should therefore be negligible. This was confirmed by using a solution of glucose (1·8 g per 100 ml) and sodium metabisulphite, $Na_2S_2O_5$ (0·03 g per 100 ml), at pH 3·5. After equilibrium had been attained, this solution contained 181 p.p.m. of total sulphur dioxide,[7] 157 p.p.m. of free sulphur dioxide and therefore, by difference, 24 p.p.m. of combined sulphur dioxide; the dissociation blank value obtained during the second 15 minutes was only 0·3 p.p.m. With a similar solution containing ten times as much sodium metabisulphite, the dissociation blank value was 5 p.p.m. in the presence of 1590 p.p.m. of free and 218 p.p.m. of combined sulphur dioxide. The effect of the dissociation of glucose bisulphite on the determination of free sulphur dioxide in ciders and similar beverages can therefore be neglected, but it may be significant in products with a high concentration of glucose or of free sulphur dioxide.

It appears, therefore, that the blank value due to dissociation of combined sulphur dioxide in ciders is not, in the main, attributable to acetaldehyde or glucose. Pyruvic acid certainly yields a dissociation blank value, as probably do other carbonyl compounds, since ciders having a relatively low content of pyruvate can give blank values up to 8 p.p.m. of sulphur dioxide. Numerous determinations of free sulphur dioxide in different ciders have shown blank values ranging from 1 to 10 p.p.m., the higher values being obtained in the presence of relatively high concentrations of sulphur dioxide bound to unidentified carbonyl compounds.

For a given cider with incremental additions of sulphur dioxide, the size of the blank value increases with increasing concentration of free sulphur dioxide. Results obtained on a commercial cider were—

Apparent content of free sulphur dioxide (tube A), p.p.m.	3·6	11·6	30·4	54·6	90·0
Blank value (tube A′), p.p.m.	1·5	2·8	4·3	5·8	7·3
Corrected content of free sulphur dioxide (A − A′), p.p.m.	2·1	8·8	26·1	48·8	82·7

Although the blank value corrections may be small, they frequently represent more than 10 per cent. of the apparent free sulphur dioxide content, especially at low concentration.

EFFECT OF TEMPERATURE ON THE FREE SULPHUR DIOXIDE CONTENT OF CIDERS—

The equilibrium between free and bound sulphur dioxide in solution is influenced by temperature. If a cider is heated the "bisulphite compounds" tend to dissociate, liberating free sulphur dioxide; conversely, if it is cooled, the carbonyl compounds react further, lowering the concentration of free sulphur dioxide. The size of this effect may be considerable: for example, the free sulphur dioxide content of a cider was found to increase from 26 p.p.m. at 20° C to 42 p.p.m. at 40° C.

The rate at which these changes occur has not yet been studied, but it is obviously a wise precaution to keep the sample at the appropriate temperature until just before analysis. Thus, it would be wrong to analyse a sample that had been stored overnight in a refrigerator if the results are intended to relate to equilibrium conditions at some other temperature.

REPRODUCIBILITY—

Six replicate determinations of free sulphur dioxide were made on two ciders. In the first, results ranged from 13·4 to 13·9 p.p.m. with a coefficient of variation of 1·4 per cent. In the second, the range was 57·5 to 58·7 p.p.m. with a coefficient of variation of 0·8 per cent.

COMPARISON WITH A METHOD FOR SOFT DRINKS—

After this manuscript was submitted, Lloyd and Cowle[13] published a method for determining free sulphur dioxide in soft drinks that is similar to ours and to the earlier methods of Kielhöfer and Aumann[5] and Paul.[6] The essential differences between these methods are listed below.

Desorption of sulphur dioxide—In the methods of Lloyd and Cowle, Kielhöfer and Aumann and Paul the sulphur dioxide is desorbed in a fast stream of carrier gas at atmospheric pressure. Our method of desorption *in vacuo* is quicker and more efficient, and therefore facilitates the application of a correction for the dissociation blank value.

Absorption of sulphur dioxide—Lloyd and Cowle absorbed the sulphur dioxide in 0·1 N potassium hydroxide in 10 per cent. v/v glycerol, since they found that absorption in neutralised hydrogen peroxide and titration with sodium hydroxide gave poor end-points with screened methyl orange. This is contrary to our experience, and no such difficulty is mentioned by Kielhöfer and Aumann or by Paul. We obtained sharp end-points provided the solutions were made up in good quality distilled water; poor end-points can occur with some samples of water de-mineralised by ion exchange.

The use of an alkaline absorbent (with subsequent acidification and titration with iodine) involves the risk of loss of sulphur dioxide in the absorption tube by oxidation. This is overcome by adding glycerol as an anti-oxidant and using oxygen-free nitrogen as the carrier gas; it is also necessary to de-aerate the apparatus by passing nitrogen for 5 minutes before adding the sample. In our proposed method, no such precautions are required since the sulphur dioxide is stable to oxidation in dilute orthophosphoric acid (pH 1 to 1·5) and is deliberately oxidised by hydrogen peroxide in the absorption tubes.

Dissociation of bound sulphur dioxide—Lloyd and Cowle state that after the desorption period of 15 to 20 minutes no subsequent dissociation of sulphur dioxide of any significance was observed. Thus, they make no correction for a dissociation blank value; this probably reflects the fact that glucose was the main binding agent for sulphur dioxide in their samples. With ciders a correction for the dissociation of bound sulphur dioxide is essential for accurate determinations.

Reproducibility—From an examination of the results of duplicate analyses shown in Table V of their paper, we judged that Lloyd and Cowle's procedure of desorption and trapping is less reproducible (coefficient of variation 2·85 per cent.) than our method.

Colorimetric modification—For samples having a low content of free sulphur dioxide, Lloyd and Cowle absorb the sulphur dioxide in sodium tetrachloromercurate and determine it colorimetrically. In our method it is possible to determine as little as 5 to 10 p.p.m. of free sulphur dioxide with sufficient accuracy for most purposes ($\pm$0·3 p.p.m.) by the normal procedure.

Conclusions

Although Lloyd and Cowle's procedure may be satisfactory for soft drinks with a relatively high content of free sulphur dioxide and low dissociation blank, it is not suitable for products for which the dissociation blank value is appreciable compared with the free sulphur dioxide content. On the other hand, our method would appear to be equally applicable to soft drinks and, if the dissociation blank value can be omitted for such products, is quicker as well as being more precise and easier to manipulate.

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Determination of Sulphur in Plant Material

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A turbidimetric procedure is described for determining sulphur in dried plant materials. Wet-digestion of the sample followed by a turbidimetric determination of the barium sulphate is suitable for routine determinations, and for samples of low sulphur content. Optimum conditions for the determination are described.

As part of an extensive study of the mineral nutrition of plants, the total sulphur content of leaves was considered to be interesting.

It is well known that sulphur is a constituent of a number of plant compounds. Interactions of sulphur and certain other nutrients have been studied,[1] and important relations found. In a recent paper, Duval[2] reviewed the importance of sulphur in agriculture.

The analytical methods for determining sulphur in plants may be broadly classified into three groups: gravimetric, volumetric and colorimetric methods. The first procedure is laborious and time-consuming for routine work, and most of the volumetric methods are not entirely satisfactory owing to the difficulty of distinguishing the end-point of the titration. These two groups of methods have been recently reviewed.[3] A critical review, by Burriel and Gómez,[4] of the colorimetric methods led us to consider that they are the most appropriate for routine purposes. The best of these methods seem to be the turbidimetric techniques based on the precipitation of sulphates with barium chloride solution and subsequent measurement of the turbidity. The main difficulty of this method lies in the selection of an appropriate stabiliser to maintain, at least temporarily, a colloidal and reproducible precipitate of barium sulphate. When we applied the stabilising mixtures proposed by Singer,[5] Butter and Chenery[6] and Krober and Howell,[7] we found that the results were erratic, problably because of our different operating conditions.

We decided to try to overcome these difficulties by using Tween-type surface-active substances. Blanc, Bertrand and Liandier[8] had previously applied this type of compound to the determination of sulphates in water, biological liquids, and wines.

The main purpose of this investigation was to find a technique that had high sensitivity (for determining the fairly small amounts of sulphur frequently found in plant materials), and was rapid enough for routine work.

Method

Reagents—

Standard sulphur solution—Dissolve an appropriate amount of analytical-reagent grade potassium sulphate in water, and adjust the volume to give a solution containing 0·4 mg of sulphur per ml.

Barium chloride solution—A solution containing 100 g of analytical-reagent grade barium chloride, $BaCl_2.2H_2O$, in 1 litre of water.

Tween-80—Obtainable from Schuchardt AG.

Barium chloride - Tween-80 *reagent*—Dissolve 20 ml of Tween-80 in 80 ml of the barium chloride solution with vigorous shaking. This solution should be prepared at least 24 hours before use.

Perchloric acid, sp.gr. 1·69.

Acid mixture—Mix 40 ml of perchloric acid and 60 ml of nitric acid, sp.gr. 1·40.

Ammonium metavanadate—A solution in perchloric acid containing 1·5 mg of vanadium per ml.

Potassium dichromate solution—An aqueous solution containing 30 mg of anhydrous potassium dichromate per ml.

APPARATUS—

We used a Hilger - Spekker absorptiometer equipped with 4-cm cells and a red filter.

Wet-decomposition apparatus—Precise details are given in the paper published by Bethge.[9] Fig. 1 shows the design of this apparatus.

PROCEDURE—

Digestion of the sample—Place 0·500 g of the ground and dried plant material in the flask, A. With the stopcock, B, closed, introduce 1 ml of the ammonium metavanadate solution, 0·5 ml of the potassium dichromate solution, and 5 ml of the acid mixture into the reflux receiver, C. Assemble the condenser, D, the flask A and the scrubber, E, as shown in Fig. 1. Fill the scrubber with a few millilitres of water, or 3 per cent. hydrogen peroxide solution. Open stopcock B, and heat flask A. Heat for five minutes, close stopcock B, and then continue until all the nitric acid has been collected in trap C, and the residue in flask A is red.

Leave the apparatus to cool for five minutes after the sample has been completely oxidised. Open stopcock B, and allow the liquid in trap C to flow into flask A. Boil the solution for a minute to rinse the apparatus, then close stopcock B, and distill most of the nitric acid into trap C until the residue in flask A is red. Allow the apparatus to cool.

Remove the reaction flask A, and wash it with a little water. Transfer the solution to a 100-ml volumetric flask by means of a teat pipette of about 10-ml capacity. Wash the flask with four or five separate 10-ml portions of water, and transfer the washings to the volumetric flask and dilute to the mark with water.

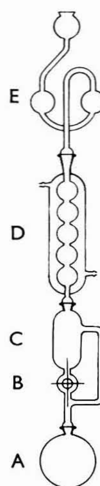

Fig. 1. Wet-decomposition apparatus

STANDARDS—

Measure 0·5, 1·0, 1·5, 2·0 and 2·5 ml of standard sulphur solution into separate 100-ml volumetric flasks. Add 2 ml of perchloric acid and 0·5 ml of potassium dichromate solution to each flask. Dilute the solutions to the mark with water.

TURBIDIMETRY—

Place 20 ml each of standard and digested sample into separate 50-ml graduated flasks, and add about 20 ml of water and 5 ml of barium chloride - Tween-80 reagent. Dilute the solutions to the mark with water, mix and measure the optical density after 30 minutes. Use a solution prepared from the same amounts of the reagent for the blank experiment.

Plot a graph relating optical density to amount of sulphur present. This graph should be linear.

DISCUSSION OF METHOD

DIGESTION OF THE SAMPLE—

The wet-oxidation of plant materials before analysis by using perchloric acid is considered valuable for most elements. Wet-digestion for sulphur determination in biological samples was proposed by Bethge.[10] The technique is of special interest, because he has shown that recoveries of sulphur were quantitative in organic substances similar to those present in plants.

With this fact in mind, the sulphur content of olive leaves was assayed by Bethge's method and a parallel assay was made with the addition of ammonium metavanadate as proposed by Smith.[11]

TABLE I

PERCENTAGE SULPHUR FOUND IN DRIED PLANT MATERIAL*

	Bethge method	Bethge method with vanadium added
Sample 1	0·12	0·15
Sample 2	0·09	0·13
Sample 3	0·09	0·14

* Mean of three replications.

The results shown in Table I indicate that to achieve a complete oxidation of organic matter, it is necessary to add vanadium as a catalyst. We followed Smith's suggestion,[11] and added dichromate as an indicator to establish the completion of the oxidation.

The time required for complete oxidation is shortened by the presence of vanadium. In its absence heating should be continued much longer, with a consequent risk of losing sulphur. This fact is in agreement with Bethge,[10] who states that some organic substances of low molecular weight are resistant to oxidation. For example, among low molecular weight sulphur-containing substances in plants, the amino-acid, methionine, is commonly found in plants.

TURBIDIMETRY—

Use of different kinds of Tween—Tween-20 (polyoxyethylene sorbitan monolaurate) and Tween-80 (polyoxyethylene sorbitan mono-oleate) have been used as stabilisers of the barium sulphate precipitate.

Fig. 2 shows changes in the optical densities that can be presumably attributed to different physical conditions of the colloidal precipitate produced by the dispersing agents. (Operating conditions were as given under "Procedure".)

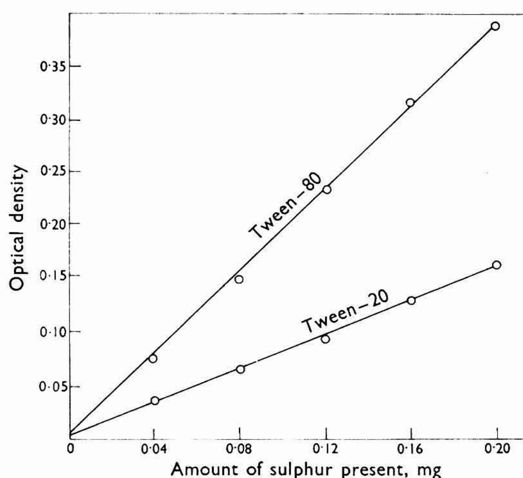

Fig. 2. Effect of Tween-20 and -80 on the optical densities of barium sulphate precipitates

In addition, the sulphur concentration interval for linearity of the standard curve is shorter when Tween-80 is used than that suggested by Blanc, Bertrand and Liandier,[8] when they used Tween-20 (see Fig. 3). (We used the operating conditions of Blanc's method.) However, the fact that there is the increased sensitivity for Tween-80 over Tween-20 (see Fig. 2), is of primary importance.

Effect of ageing of reagent solutions—A fresh solution of the barium chloride - Tween-80 reagent was prepared and added at intervals to a solution containing 0·6 mg of sulphur per 100 ml.

A comprehensive study of the ageing of solutions of barium chloride has been made by Bogan and Moyer.[12]

Ageing of reagent solutions caused an increase in the optical densities, and the effect of ageing appeared to be complete in 24 hours. The results are given below—

Time after reagent preparation, hours	0·5	1	3	6	24	48	96
Optical density	0·256	0·261	0·263	0·262	0·301	0·304	0·304

Reagent concentration—Different amounts of barium chloride - Tween-80 reagent were added to several solutions containing 0·6 mg of sulphur per 100 ml. It is clearly shown below that the complete precipitation of barium sulphate requires a quantity of reagent in excess of 3 ml, but the excess is not critical—

Reagent added, ml	1	2	3	4	5
Optical density	0·252	0·290	0·304	0·302	0·305

Perchloric acid concentration—Different amounts of perchloric acid were added to five solutions containing 0·12 mg of sulphur in a volume of 50 ml. From the results given below, it can be seen that the optical density is affected only slightly when the perchloric acid concentration is increased fivefold—

Perchloric acid added, ml	0·1	0·2	0·3	0·4	0·5
Optical density	0·240	0·245	0·245	0·250	0·250

Stability of barium sulphate suspension—The results given in Table II show the optical density values, at intervals, for a number of colloidal suspensions of barium sulphate whose sulphur content varies. The suspensions were shaken vigorously, and the optical densities were measured in 1-cm cells with a Beckman DU spectrophotometer.

TABLE II

STABILITY OF SUSPENSION

$\lambda = 410\ m\mu$

Sulphur content, mg of sulphur per 100 ml	Optical density after—				
	25 minutes	1 hour	2 hours	5 hours	20 hours
0·4	0·042	0·043	0·046	0·044	0·037
0·8	0·098	0·100	0·102	0·100	0·093
1·2	0·170	0·173	0·174	0·175	0·162

It can be seen that the optical density can be read over a long period of time.

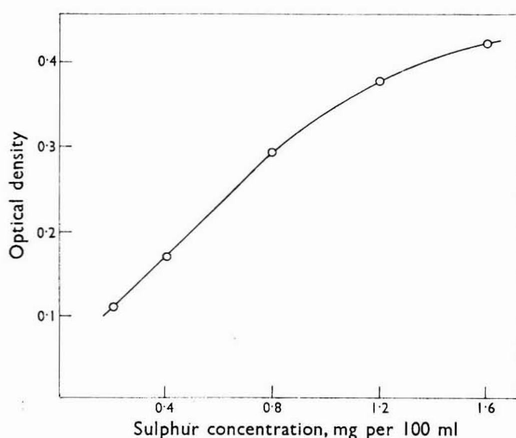

Fig. 3. Linearity of the standard sulphur-concentration curve, when Tween-20 was used as stabiliser

Standards—Two series of standards were prepared. The first, by using the wet-combustion method described under "Procedure"; 0·500 g of reagent-grade cellulose powder and a measured quantity of potassium sulphate solution, as a source of sulphur, were placed in the reaction flask. The second standard was prepared by adding the same quantities of potassium sulphate that were used in the preparation of the first standard, 2 ml of perchloric acid and 0·5 ml of potassium dichromate solution, to the 100-ml reaction flasks.

The results obtained by both methods are shown in Table III. The Beckman DU spectrophotometer was used for optical-density measurements.

TABLE III

RESULTS OBTAINED FOR STANDARDS

($\lambda = 410$ mμ)

Sulphur content, mg of sulphur per 100 ml	Optical density after— wet-oxidation	no oxidation
0·2	0·024	0·027
0·4	0·051	0·050
0·6	0·073	0·076
0·8	0·100	0·103
1·0	0·126	0·126

ANALYTICAL RESULTS

The *accuracy* of the turbidimetric method was examined by adding known amounts of sulphur, as potassium sulphate, to a digested sample of olive leaves. The results are given below—

Sulphur added, mg*	0·1	0·2	0·3	0·4
Sulphur found, per cent.	102·3	99·0	99·1	100·0

* In addition to the sulphur added, the solution contained 77 mg from the digested sample.

The *precision* of the proposed turbidimetric method is shown below—

Percentage sulphur	0·100, 0·102, 0·102, 0·103, 0·102, 0·103 0·103, 0·103, 0·100, 0·102, 0·104, 0·104
Mean	0·102
Coefficient of variation	1·32 per cent.

The results shown in Table IV further illustrate the precision that may be expected for a number of samples of widely varying sulphur contents.

TABLE IV

PRECISION AS FUNCTION OF SULPHUR CONTENT OF SAMPLE

Sample No.	Nature of sample	Sulphur per cent.	Standard deviation	Coefficient of variation, %	95 per cent. confidence limits‡
1	Olive	0·087*	$2·00 \times 10^{-3}$	2·30	0·085 to 0·089
2	,,	0·103†	$1·41 \times 10^{-3}$	1·37	0·101 to 0·105
3	,,	0·116*	$3·61 \times 10^{-3}$	3·11	0·111 to 0·121
4	Bean	0·119†	$4·24 \times 10^{-3}$	3·56	0·112 to 0·126
5	Olive	0·124†	$3·65 \times 10^{-3}$	2·94	0·118 to 0·130
6	,,	0·137†	$1·15 \times 10^{-3}$	0·84	0·135 to 0·139
7	,,	0·171*	$3·28 \times 10^{-3}$	1·92	0·168 to 0·175
8	,,	0·178†	$5·92 \times 10^{-3}$	3·33	0·169 to 0·187
9	Orange	0·211*	$4·27 \times 10^{-3}$	2·02	0·206 to 0·216
10	Sugar cane	0·551*	$14·92 \times 10^{-3}$	2·71	0·532 to 0·570

* Mean of five replications.
† Mean of four replications.
‡ For mean at 5 per cent. level, confidence limit = mean $\pm\ t\ \dfrac{\sigma}{\sqrt{n}}$; t for 4 degrees of freedom = 2·78; t for 3 degrees of freedom = 3·18.

The confidence limits are of interest because they make it possible to decide the limits of sensitivity. For example, samples 3 and 4 cannot be distinguished, because the true population mean lies between almost the same limits: 0·111 to 0·121 per cent. of sulphur for sample 3 and 0·112 to 0·126 per cent. for sample 4, with a 95 per cent. confidence limit. It is also apparent that it is not possible to state unequivocally that samples 4 and 5, and 7 and 8 differ in sulphur content, because the upper confidence limits of samples 4 and 7 are greater than the lower limits of samples 5 and 8, respectively. It is reasonable to assume,

however, that the sulphur contents of samples 8, 9 and 10 are different from each other, and from the others shown in Table IV, because the 95 per cent. confidence limits do not overlap.

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The Determination of Propylene Glycol in Tobacco by Cellulose-column Chromatography

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The cellulose - carbon column method for the quantitative determination of glycerol in tobacco has been extended to the determination of propylene glycol, which is occasionally found in tobacco, either as the sole humectant or in small amounts associated with added glycerol. Glycerol and propylene glycol can both be accurately determinated in the presence of each other, in a single experiment.

In an earlier paper,[1] procedures were described for the qualitative and quantitative determination of glycerol in tobacco. In the course of the qualitative detection of glycerol, the presence of propylene glycol was occasionally clearly indicated, and in this paper an extension of the column method is described, so that propylene glycol detected by the paper-chromatographic procedure[1] can be accurately determined. In this paper, only modifications of the earlier procedure[1] will be described in any detail.

The first portion of eluate from the cellulose - carbon column contains all the propylene glycol, accompanied by a small portion of the glycerol (see Fig. 1).

The method developed is for determining propylene glycol and glycerol based on collection of the eluate in two portions; the propylene glycol and some of the glycerol are determined in the first portion, and the remainder of the glycerol in the second. When attempts to determine glycerol and propylene glycol in a single 500 ml of eluate were made, interference in the estimation of propylene glycol arose from the material responsible for the "apparent glycerol" blank value of the tobacco. In the proposed method, however, this interference becomes significant only in the second fraction, containing glycerol alone, and the added glycerol may be calculated by subtracting the appropriate "apparent glycerol" blank value for the unmanufactured tobacco; some experimentally determined blank values are listed in Table II of the earlier paper.[1] In addition, inaccuracies arose when a suitable portion of a single 500 ml of eluate was analysed for a small quantity of propylene glycol in the presence of a large excess of glycerol, since the determination of propylene glycol depended on a small difference between two larger titrations; this possible error is minimised when the first part of the eluate, containing a relatively small proportion of glycerol, is analysed separately for propylene glycol.

Experimental

Experiment has shown that the optimum conditions for accuracy require the collection of an initial 200 ml of eluate, followed by a further 400 ml. The glycerol content of the 200-ml portion increases with temperature; for example, it is approximately 10 per cent. of the total glycerol present at 15° C and 20 per cent. at 25° C.

The glycerol is determined in the 200-ml portion of the eluate in the presence of the propylene glycol, by making use of the fact that when glycerol is oxidised with periodate it yields formic acid (which can be titrated with alkali) and formaldehyde, but propylene glycol only yields aldehydes.[2,3] The propylene glycol content is determined by measuring the total periodate consumed, less that required to oxidise the glycerol; the glyercol in the 400-ml portion of eluate is most readily determined by measuring the total periodate used.

It is necessary to remove all the solvent from the eluate before oxidising the glycerol and subsequently determining the formic acid. The titration cannot be carried out in the presence of ether, which removes the indicator from the aqueous layer, and in the presence of alcohol low results are obtained. The solvents are most conveniently removed by evaporation on a steam-bath; no loss of glycerol occurs, and propylene glycol, which may be lost to some extent, is determined on a separate portion of eluate without removal of the solvent.

None of the many methods available[4 to 10] for determining glycerol by acidimetric titration of the formic acid produced by periodate oxidation proved entirely suitable; most were designed for amounts of glycerol greater than the milligram or less present in the eluate, and, for simplicity, a titration in which an indicator was used was preferred to an electrometric end-point measurement. Potassium periodate was used as the oxidant, and the amount of sulphuric acid added when preparing the solution was kept to a minimum to keep the blank value of the acidimetric titration as low as possible; this modification gave satisfactory results in the procedure for determining total periodate used. It is better

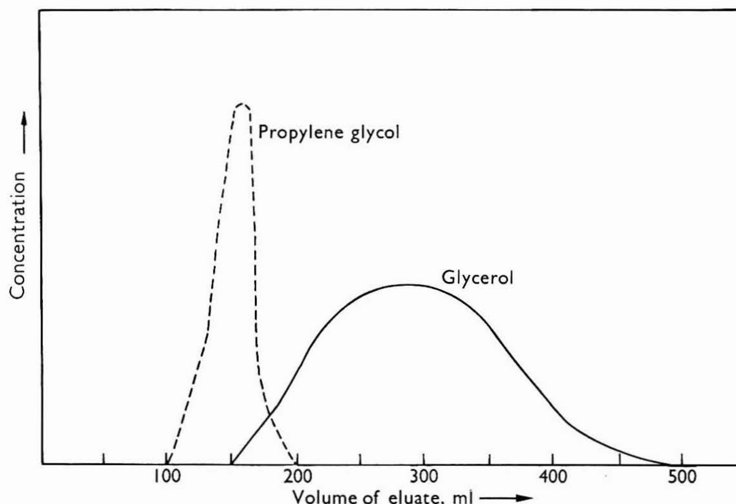

Fig. 1. Curve illustrating the recovery of propylene glycol and glycerol. (Column temperature, 17° C)

not to oxidise with neutral solutions as recommended by Neuburger and Bruening,[8] since neutral solutions prepared with the reagent we used (analytical-reagent grade potassium periodate) gave an inconvenient negative blank value. We tried bromocresol purple,[8] bromothymol blue,[5] phenol red[7] and methyl red[3] as indicators, and preferred bromocresol purple. The excess of periodate was destroyed with ethylene glycol, as recommended by Erskine, Strouts, Walley and Lazarus.[7]

METHOD

The preparation of the column, extraction of the sample and its transfer to the column are described in the previous paper.[1]

ADDITIONAL REAGENTS—

Potassium periodate solution—Dissolve 1·15 g of analytical-reagent grade potassium periodate in about 600 ml of hot water that has been boiled to expel carbon dioxide, cool, add 7 ml of 0·1 N sulphuric acid and dilute to 1 litre with carbon-dioxide-free water.

Sodium hydroxide solution, approximately 0·02 N—Prepare in carbon-dioxide-free water.

Sulphuric acid, 0·02 N.

Bromocresol purple solution, 0·1 *per cent. w/v in* 95 *per cent. ethanol.*

Ethylene glycol solution, approximately 10 *per cent. v/v, aqueous.*

COLLECTION OF THE ELUATE FROM THE COLUMN—

Collect the first 200 ml of eluate into a 200-ml graduated flask, and the next 400 ml of eluate into a 500-ml graduated flask containing initially 100 ml of solvent mixture.

ANALYSIS OF THE FIRST 200 ml OF ELUATE—

To make the maximum use of this eluate, transfer by means of a pipette a further 2 ml of solvent mixture into the graduated flask, and thoroughly shake the flask. This facilitates duplicate determinations on 50-ml portions.

Determination of total periodate used—Transfer 50 ml of the eluate to a 500-ml conical flask fitted with a ground-glass socket, and proceed as directed under "Procedure for oxidising glycerol with periodate" in the earlier paper.[1] A sufficient excess of potassium periodate must be maintained; if the difference in titre between blank value and sample exceeds 4 ml, the oxidation should be repeated using a smaller portion of eluate.

Determination of glycerol—By pipette transfer 50 ml of the eluate (or a smaller portion, if this was necessary for determining the total periodate used) into a 250-ml beaker, add 70 ml of water, and evaporate on the steam-bath until approximately 25 ml of solution remain. Cool and transfer, with the aid of distilled water, to a 500-ml conical flask, fitted with a ground-glass socket, so that the final volume is approximately 100 ml. Add 1 ml of 0·02 N sulphuric acid, boil for 5 minutes, close the flask with a rubber stopper carrying a soda-lime guard tube and cool to room temperature. Add 0·2 ml of bromocresol purple solution, titrate with 0·02 N sodium hydroxide until the first distinct purple colour appears and add 25 ml of the potassium periodate solution from a pipette. Mix, close the flask with a glass stopper, and set aside in the dark at room temperature for 40 minutes. Add 0·5 ml of 10 per cent. ethylene glycol, mix, set aside for a further 20 minutes, and titrate with 0·02 N sodium hydroxide until the same distinct purple colour appears. Carry out a blank determination, at the same time, on 100 ml of water.

The sodium hydroxide solution should be standardised by titrating it against 0·02 N sulphuric acid with bromocresol purple as indicator.

If necessary, rinse down the flask during the titration with carbon-dioxide-free water that has been titrated with the sodium hydroxide solution until the first distinct purple colour appeared.

NOTES—

1. The solution obtained by simple evaporation of the eluate may occasionally be so cloudy that the end-point of the titration is obscured; this can be avoided by separating off the ether layer before evaporation: 50 ml of the eluate should be shaken with 50 ml of water, and then a further 15 ml of water, and the combined aqueous layers transferred to the 250-ml beaker and evaporated on a steam-bath before oxidation as described above.

2. The purple colour of the end-point changes fairly rapidly to a bluish-grey colour. A lasting purple end-point colour can be obtained, if preferred, by passing nitrogen into the flask during the titration; duplicate determinations, made in the presence and absence of nitrogen, were satisfactory, and detection of the end-point in the absence of nitrogen was not difficult.

ANALYSIS OF THE FINAL 400 ml OF ELUATE—

The glycerol in this solution is most conveniently determined on a 50-ml portion by the iodimetric procedure referred to above for determining total periodate used.

Calculation of glycerol and propylene glycol—

1 ml of 0·02 N sodium hydroxide ≡ 1·84 mg of glycerol.

1 ml of 0·05 N sodium thiosulphate ≡ 1·90 mg of propylene glycol or 1·15 mg of glycerol.

Example—

Determination made on 1 g of tobacco.

If V is the sodium hydroxide titre for 50 ml of the 200 ml eluate (diluted to 202 ml)

$$\text{Glycerol content} = 1{\cdot}84 \times \frac{202}{50} V \text{ mg in the 202 ml}$$

and sodium thiosulphate equivalent of the glycerol content of the 50 ml eluate $= \frac{1{\cdot}84}{1{\cdot}15} \times V$.

If v_1 is the sodium thiosulphate titre (blank titre *minus* sample titre) for 50 ml of the 202-ml eluate, the sodium thiosulphate equivalent of propylene glycol content in the 50 ml aliquot is given by—

$$v_1 - \frac{1{\cdot}84}{1{\cdot}15} \times V$$

$$\text{Propylene glycol content} = \left(v_1 - \frac{1{\cdot}84}{1{\cdot}15} V\right) \times 1{\cdot}90 \times \frac{202}{50} \times \frac{1}{10} \text{ per cent.}$$

If v_2 is the sodium thiosulphate titre (blank value) for 50 ml of the 400 ml eluate (diluted to 500 ml)—

$$\text{Glycerol content} = 1{\cdot}15\, v_2 \times 10 \text{ mg in the 500 ml}$$

$$\text{and} \quad \text{Total glycerol} = \left(11{\cdot}5\, v_2 + 1{\cdot}84 \times \frac{202}{50} V\right) \times \frac{1}{10} \text{ per cent.}$$

Added glycerol = total glycerol (per cent.) − x, where x is the blank value determined on unmanufactured tobacco of similar origin (see earlier paper[1]).

RECOVERY OF GLYCEROL AND PROPYLENE GLYCOL FROM TOBACCO—

Recovery experiments were carried out as described in the previous paper.[1] Accurately measured volumes of propylene glycol and glycerol solutions were added to 1 g of tobacco sample, and the glycerol and propylene glycol contents of the solutions were determined. The recoveries are shown in Table I.

TABLE I

RECOVERY OF GLYCEROL AND PROPYLENE GLYCOL FROM 1 g OF TOBACCO

Glycerol added, mg	Propylene glycol added, mg	Glycerol recovered,* mg	Propylene glycol recovered, mg
20	10	19	10
20	5	19	5
—	15	0	15
38	—	37	0
—	39	0	39

* Corrected by subtraction of the apparent glycerol blank value ≡ 2 mg

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Identification of Aliphatic Alcohols by Pyrolysis

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A method is described for identifying volatile aliphatic alcohols by gas chromatography of their pyrolysis products. The dependence of the pyrolysis pattern upon pyrolysis temperature and gas flow-rate has been investigated. The method constitutes a sensitive technique for investigating volatile compounds of fractions eluted from gas-chromatographic columns, and it can be applied to other volatile compounds.

PRELIMINARY identification of volatile compounds that have been separated by gas chromatography is usually carried out by measuring the retention time of a compound on two or more stationary phases. The evidence obtained by this means should be supported by such other means of identification as infrared or mass spectrometry.

The infrared spectrometric method suffers from the disadvantage that several hundred micrograms of the volatile compound are often needed for a definite identification, while the mass spectrometer, which only requires submicrograms of a compound for this purpose, is too expensive to be generally available.

However, the basic principles of the mass spectrometer, fragmentation and separation of fragmentation products, may be applied to a simple pyrolysis oven and then to the gas-chromatographic column, as suggested by Keulemans.[1] This technique is now used for identifying synthetic polymers[2] and other compounds of low volatility.[3]

In this paper, a method is described for similar identification of more volatile compounds, eluted from gas-chromatographic columns, using aliphatic alcohols as test substances.

METHOD

APPARATUS—

A Pye Argon gas chromatograph was re-equipped by replacing the β-ray detector by a hydrogen-flame ionisation detector, in accordance with the directions of Murray and Williams.[4]

The metallic thermostat parts were removed from the thermostat so that a 3-metre glass column could be inserted. The column packing consisted of Chromosorb W covered with 30 per cent. of Apiezon L. Nitrogen was used as the carrier gas at a flow-rate of 32 ml per minute, except when otherwise stated. The flame was fed by hydrogen and air.

A quartz pyrolysis tube that was 20 cm long and had an inner diameter of 2 mm was filled over a length of 10 cm with Chromosorb P and surrounded by a tubular furnace over a length of 13 cm, and then attached to the top of the column with silicone rubber tubing. The inlet system is shown in Fig. 1. By placing the stopcocks in their proper position the carrier gas could be directed either through the U-tube or directly to the column.

The compound under investigation was led into the U-tube, which was attached to the inlet system, by blowing a small amount of the vapour from a syringe. In other instances, the compound was first trapped in the U-tube at the outlet of a gas-chromatographic column. The U-tube thus forms part of a second apparatus used for analysing the components of odours.

The alcohols used in the following experiments were obtained from British Drug Houses Ltd., or from Fluka A.G. The alcohols were found to be 97 to 99·9 per cent. pure by gas chromatography on silicone oil, β,β'-dioxypropionitrile and tricyanoethoxypropane substrates.

PROCEDURE

The compound contained in the U-tube, usually 50 to 500 μg, was swept through the pyrolysis tube on to the gas-chromatographic column, and a chromatogram of the pyrolysis products was recorded.

Once or twice each day, a mixture of n-paraffins was run under the same experimental conditions so that the Kovats index numbers of the peaks could be calculated. This scale is based on the retention volumes of the peak-maxima of the n-paraffins, C_zH_{2z+2} (where z is

an even number); the positions of the peak-maxima are defined by the number 100z. Intermediate positions are then numbered by interpolation on a logarithmic scale. This index is independent of the material of the stationary phase, provided that non-polar phases are used,[5] and appears to have a theoretical foundation.

The n-paraffins did not show an appreciable pyrolytic breakdown at the temperatures used in these experiments. The Kovats index and the relative peak areas of the pyrolysis products were drawn as a histogram to give a clear picture of the final results. The peak area of the chromatogram was estimated by multiplying retention time and peak height. The main peak of each histogram was always set at 100 and the other peak areas of the histogram were calculated as fractions of this main peak area.

The determination of the peak area is in most instances approximate, since many of the peaks were not completely separated and only a rather rough estimate of the peak height could be made in these instances.

Results

Results obtained from pyrolysis of a number of primary, secondary and branched-chain aliphatic alcohols are shown in Fig. 2. Peaks whose retention index lies below 300 are

Table I: Indices of main peaks and corresponding olefins

Alcohol	Corresponding olefin	Boiling-point, °C	Index from boiling-point	Index found
n-Pentanol	Pent-1-ene	40	511	510
	Pent-2-ene	36·5	502	—
n-Hexanol	Hex-1-ene	64	587	—
	Hex-2-ene	67	595	—
	Hex-3-ene	70	605	605
Hexan-2-ol	Hex-1-ene	64	587	—
	Hex-2-ene	67	595	—
	Hex-3-ene	70	605	607
2-Methylpentan-1-ol	2-Methylpent-1-ene	60·7	576	—
	2-Methylpent-2-ene	67·3	595	592

not given, since they could not be calculated with sufficient accuracy. The index of the main peak obtained from the pyrolysis of an alcohol was always found to correspond to that of an olefin with the same carbon skeleton as the alcohol. This can be seen from Table I, which presents the indices of olefins that can be expected to be formed from some of the alcohols tested. The indices for the olefins were calculated from their boiling points.[5] These

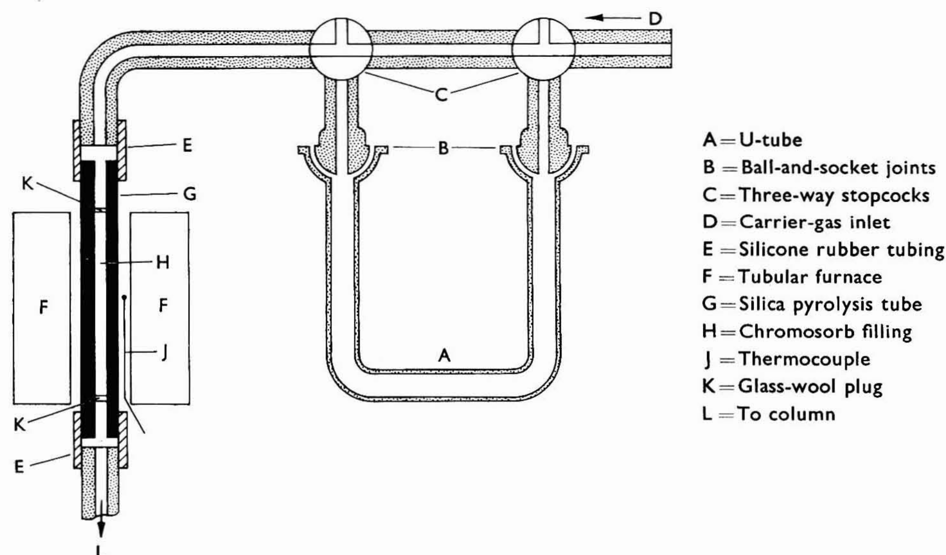

Fig. 1. Injection system and pyrolysis unit

indices are compared, and one of them is seen to correspond with the indices of compounds actually obtained from the chromatograms obtained in the manner described above.

In addition, infrared analysis, with katharometer detection, of compounds trapped in separate experiments showed the presence of these olefins in the pyrolysis products of the alcohols, whenever these confirmatory experiments were performed.

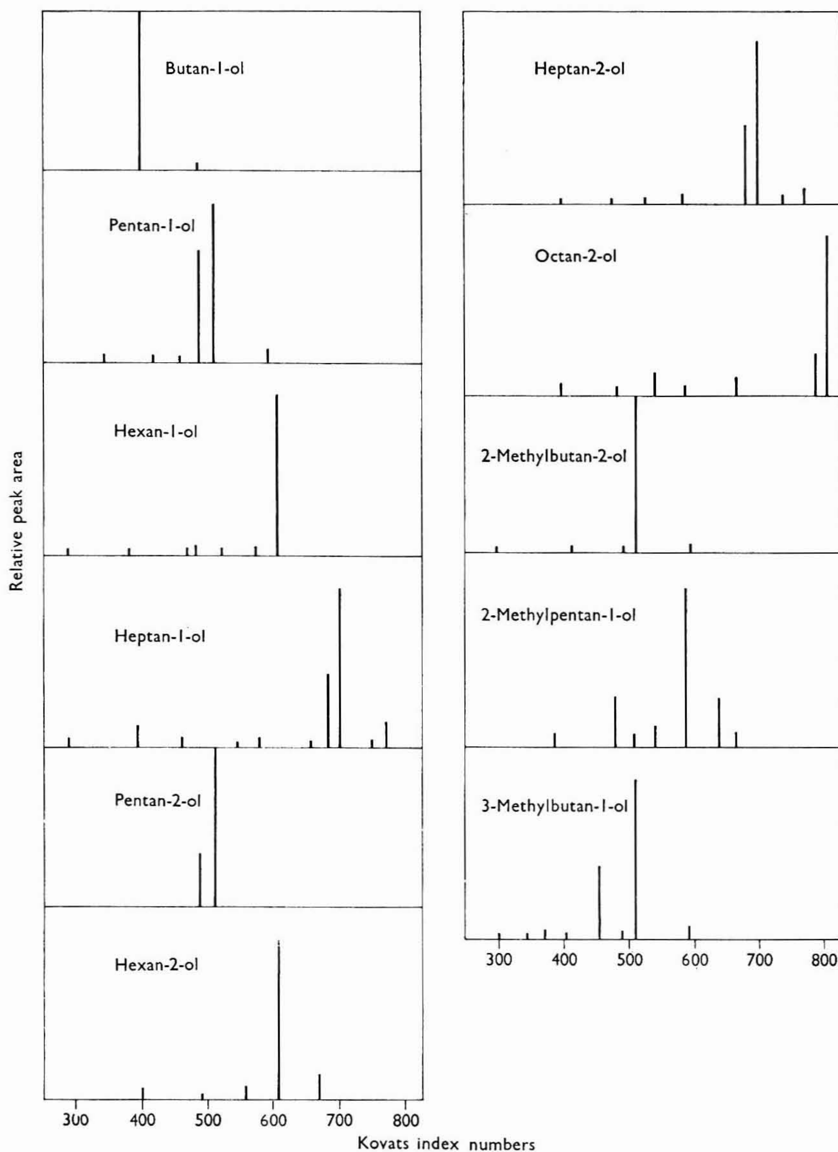

Fig. 2. Pyrolysis patterns of some aliphatic alcohols

A number of experiments were carried out to study the influence of change of pyrolysis temperature. Table II shows some of the results obtained; they are representative of all alcohols tested.

It can be seen that the products of pyrolysis do not differ markedly when pyrolysis temperatures change from 470° C to 560° C, even though their relative quantities change

TABLE II: PYROLYSIS OF ALCOHOLS AT DIFFERENT TEMPERATURES

	Pyrolysis temperature			
	560° C		470° C	
Alcohol	Index	Relative peak area	Index	Relative peak area
		(14 experiments)		(6 experiments)
Pentan-1-ol	347	2·31	—	—
	421	4·1	—	—
	462	1·2	460	1·4
	491	72·2	489	68·3
	510	100	509	100
	594	9·2	596	2·4
		(21 experiments)		(6 experiments)
3-Methylbutan-1-ol	307	2·34	297	1·09
	345	3·66	—	—
	371	8·2	—	—
	403	3·06	398	4·62
	456	49·0	455	72·0
	490	1·52	487	1·60
	512	100	510	100
	594	6·1	592	9·00

TABLE III: REPRODUCIBILITY OF INDEX NUMBERS AND RELATIVE PEAK AREAS

Index numbers, mean of 21 experiments	Standard deviation of a single observation	Relative peak areas, mean of 21 experiments	Standard deviation of a single observation
307	2·8	2·34	0·28
345	2·2	3·66	0·75
371	2·0	8·2	2·70
403	2·9	3·06	1·00
456	1·7	49·0	5·1
490	1·7	1·52	0·04
512	1·9	100	0
594	2·3	6·1	1·4

Test compound: 3-methylbutan-1-ol. Pyrolysis temperature: 560° C. Number of experiments: 21.

slightly. At temperatures below 400° C increasing amounts of the alcohol passed unaltered through the pyrolysis tube. In a few experiments at 700° C, little change from results obtained at lower temperatures was observed. Table III gives some indication of the reproducibility of the method.

It can be seen that Kovats indices are reproducible to within a few index units. In separate experiments, column length, amount of stationary phase on the support and column temperature (lowest 40° C, highest 120° C) were varied, but not found to affect the index number.

The main error in determining peak areas was caused by the fact that not all peaks were satisfactorily separated on our column. However, a relative variation in peak area of even 25 per cent. does not impair the usefulness of the method for its purpose of compound identification. It is to be expected that the reproducibility will be much better on columns of high separating power, *e.g.*, capillary columns.

The possibility that changes in the carrier-gas flow-rate would affect the ratio of pyrolysis products, because of changes in the contact time of the compound with the hot pyrolysis-oven filling, proved unfounded. Such ratio changes did not exceed those found when the gas flow-rate was varied between 20 and 60 ml per minute.

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SHORT PAPERS

Examination of Detergents by Paper Chromatography, Part II*

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A SOLVENT based on ethyl acetate develops paper chromatograms of detergents much faster than the solvent described recently in this journal.[1] A ninhydrin spray provided a useful additional test for some nitrogenous compounds.

SOLVENTS

A solvent mixture of ethyl acetate, methanol and ammonia solution, sp.gr. 0·88, in the proportions, 60 + 15 + 5, recommended by Gasparič, Borecký, Obruba and Hanslík,[2] for the paper chromatographic determination of ethanolamines, gives separations of detergent components similar to those obtained when t-butanol is used as solvent, but the mixture of solvents flows more evenly and quickly. Development is complete in 2 to 3 hours, compared to the 17 to 18 hours previously required. Some approximate R_F values, obtained by using an ethyl acetate, methanol and ammonia solution (60 + 15 + 5) mixed solvent, were—

Substance	Anionic surface-active agents*	Non-ionic surface-active agents	Soaps*	Quaternaries	Toluene sulphonates	Xylene sulphonates	Urea
R_F value	0·70	0·95	0·60	0·60	0·15	0·22	0·24

* Elongated spots

Ethyl acetate, methanol and ammonia solution, mixed in the proportions, 45 + 45 + 10, gave good and rapid separations of amines from hydrolysates. Both mixtures should be discarded after three days, because they are affected by slow hydrolysis of the ethyl acetate.

When these solvents are to be used, the paper, after washing, should be hung up to dry at room temperature and used as soon as it is dry. In this way the optimum results can be obtained, since the paper retains the correct amount of water. Heating it removes too much moisture.

NINHYDRIN SPRAY

If the paper is sprayed with a solution of ninhydrin (indanetrione hydrate), containing 0·2 g of ninhydrin in 95 ml of methanol and 5 ml of 2 N acetic acid, and then heated at 80° C for 5 minutes, purple spots are formed by primary amines. Further heating at 120° C for 10 minutes deepens the colour of the spots already formed, gives purple or blue spots with other nitrogenous substances, and gives pink spots with metals[3] (see Table I).

TABLE I

COLOUR REACTIONS OF DETERGENT COMPONENTS WITH NINHYDRIN

Approximate R_F values were obtained by using mixtures of ethyl acetate, methanol and ammonia solution as solvent

Component	R_F values; mixed solvent in proportions		Colours developed by heating at	
	60 + 15 + 5	45 + 45 + 10	80° C	120° C
Monoethanolamine	0·35	0·62	purple	deep purple
Diethanolamine*	0·42	0·71	—	purple, with white centre
Triethanolamine	0·55	0·78	—	blue
Isopropanolamine	0·50	0·71	purple	deep purple
Amine oxide	0·85	—	—	deep purple
Monethanolamide impurity	0·95	—	—	purple
Taurine	—	0·29	purple	deep purple
N-Methyl taurine*	—	0·44	—	purple
Sarcosine*	—	0·29	light purple	purple
Metal ions (Na^+, K^+)	0·00	0·02 to 0·06	—	pink

* These gave deep blue spots with acetaldehyde - nitroprusside reagent

* For details of Part I of this series see reference list, p. 76.

Monoethanolamides usually give purple spots near the solvent front after heating at 120° C. This colour is due to an impurity, because no colour is formed after purification of the amide by repeated recrystallisation from light petroleum (boiling-range, 60° to 80° C) or by treatment with ion-exchange resins. Further, a trace of a substance, having a high R_F value and giving a strong reaction with ninhydrin, is obtained by evaporating to dryness the mother liquor from the recrystallisation.

Most monoethanolamides and diethanolamides contain small amounts of the corresponding ethanolamines; these show as small spots on the chromatogram, and thus provide clues to the identity of the amide.

When ninhydrin is added to the sequence of sprays used on a single chromatogram, colours formed towards the end of the treatment are difficult to detect. To obtain clear results, similar series of spots are put on the right and left halves of the paper, and after development the paper is divided by a vertical cut. One half is examined by the method described previously,[1] while the other half is treated with ninhydrin, heated at 80° C for 5 minutes and subsequently at 120° C for 10 minutes, and then tested for secondary amines with the acetaldehyde - nitroprusside sprays.[1] Colours caused by ninhydrin do not mask the intense blue spots produced in this last test, but they do hide the weaker khaki spots formed by primary amines. Chromatograms of amide hydrolysates should be sprayed with ninhydrin followed by acetaldehyde - nitroprusside reagent (see Table I).

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Note: reference 1 refers to Part I of this series.

The Filtration of Partially Reduced Alkaline Permanganate Solutions

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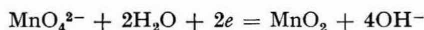
We have recently been concerned with the use of standard potassium permanganate in neutral or weakly alkaline solution for volumetric analysis. Under such conditions, manganese dioxide in an extremely finely divided state is formed as one of the products; this renders filtration by the classical techniques slow or virtually impracticable, since manganese dioxide should not be left in contact with permanganate longer than absolutely necessary as it catalyses its decomposition.

We have investigated the use of a coagulant, but the choice is limited to one that does not appreciably precipitate in the alkaline conditions that develop as a result of hydroxyl ions produced by the reaction—



$$MnO_4^{2-} + 2H_2O + 2e = MnO_2 + 4OH^-$$

Aluminium salts are therefore of no use, as large amounts of aluminium hydroxide are precipitated, further complicating the problem. We have found that the addition of 10 ml of saturated calcium sulphate solution coagulates the suspended manganese dioxide, after warming to 40° C for a few minutes. This amount of calcium sulphate solution will effectively coagulate the precipitate resulting from the reduction of 50 ml of 0·1 N permanganate.

Even so, the coagulated precipitate is extremely light and still is virtually unfilterable on either a prepared Gooch crucible or a sintered-glass crucible. We have found that the most effective method of filtration is to use a No. 4 sintered-glass crucible in which a wad of glass-wool has been placed. This causes the bulk of the precipitate to be trapped before reaching the sintered-glass filter-plate, which otherwise rapidly becomes blocked. The filtration of 100 ml of a mixture resulting from the partial reduction of 50 ml of 0·1 N permanganate was complete in 10 minutes when this technique was used, and the precipitate was easy to wash. Excess of permanganate could be determined on the clear filtrate after acidification, by any of the standard techniques.

Application of the method

The method described has proved useful for studying the oxidation of a neutral solution of sodium thiosulphate by permanganate by the procedure described below.

Add a known volume of standard 0·01 N sodium thiosulphate solution to a known excess of standard permanganate solution. Stir well, then add 10 ml of saturated calcium sulphate

solution to the mixture, and warm to 40° C. This causes immediate coagulation of the precipitate. Filter off the precipitate immediately on a No. 4 sintered-glass crucible in which a wad of glass-wool has been placed. Wash with successive small amounts of distilled water, acidify the filtrate and washings with 10 ml of syrupy phosphoric acid, and add a measured excess of standard oxalic acid. Warm to 50° C., and when the mixture becomes decolorised, back-titrate the excess of oxalic acid with standard permanganate in the usual way to the first appearance of a faint permanent pink colour.

RESULTS—

Permanganate taken = 25 ml of 0·01972 M solution.
Thiosulphate taken = 10 ml of 0·01002 M solution.
Oxalic acid added = 25 ml of 0·9128 N solution.
Back-titration = 11·70 ml of 0·01972 M permanganate solution.

CALCULATION—

From these results it can be calculated that the amount of permanganate used in the reaction is 13·36 ml of 0·02 M solution, and the amount of thiosulphate reacting is 10 ml of 0·01002 M solution

Therefore, 3 moles of sodium thiosulphate are equivalent to 8 moles of potassium permanganate, from which the reaction is shown to be—

$$3Na_2S_2O_3 + 8KMnO_4 + H_2O = 3K_2SO_4 + 3Na_2SO_4 + 8MnO_2 + 2KOH$$

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Book Reviews

MOLECULAR VIB-ROTORS: THE THEORY AND INTERPRETATION OF HIGH RESOLUTION INFRARED SPECTRA. By HARRY C. ALLEN, JUN., and PAUL C. CROSS. Pp. viii + 324. New York and London: John Wiley & Sons Inc. 1963. Price 105s.

In this volume, Dr. Allen of the National Bureau of Standards, Washington, and Dr. Cross of the Mellon Institute, Pittsburgh, provide an introduction to the theory of vibrational - rotational spectra shown by simple gaseous molecules and describe how the theory can be used to analyse the rotational fine structure revealed by modern high-resolving spectrometers. In this way, important structural information, such as the bond-lengths, bond-angles and force-constants for the various bonds in simple molecules, can be obtained. The theories presented by G. Herzberg in his classic monograph ("Infrared and Raman Spectra," 1945) are extended and brought up to date.

The treatment of the subject is of necessity largely mathematical, and assumes that the reader is familiar with the methods of quantum mechanics and with the principles of group theory; it is, nevertheless, sufficiently detailed to enable the reader not only to understand the mathematical derivations, but also to extend and adapt the methods to the solution of his own problems. The monograph is primarily designed to interest theoretical chemists and spectroscopists, who study small molecules. The average analytical chemist, who is concerned with the behaviour of complex molecules and whose approach to spectroscopy is largely empirical, is unlikely to find the volume of practical value. J. E. PAGE

THE APPLICATION OF ORGANIC BASES IN ANALYTICAL CHEMISTRY. By E. A. OSTROUMOV. Translated from the Russian by D. A. PATERSON. Pp. xxv + 159. Oxford, London, New York, Paris: Pergamon Press. 1962. Price 50s.

This book describes systematic studies made by the author over a number of years on the application of three organic bases to the analysis of inorganic materials. Methods, claimed to be accurate and rapid for separating and determining elements by means of pyridine alone, pyridine in the presence of its salts, hydrogen sulphide in the presence of pyridine, and the precipitation of metal ions by α-picoline and by hydrogen sulphide in the presence of hexamethylenetetramine, have been studied. The separations described for many cations alone or in the presence of each other are based on a close control of pH, and of pH with complex formation.

The accuracy of the many separations investigated is exemplified in tables of results obtained from synthetic solutions and their mixtures, often of only a limited range. The good results claimed for the application of these methods to minerals, rocks, and the like are, with one exception, not exemplified. Further, the behaviour of a method in the presence of a high concentration of

alkali salt, often inevitable as the result of a fusion essential for the attack of a substance, seems to have been disregarded.

The title of the book is, to some extent, misleading as only three organic bases have been considered. The printing of the text and the accompanying tables is not of a particularly high standard. There are also errors in the latter (see Tables 5, 6, 7 and 14) and in the text where "manganese" (p. 129) should be "magnesium" and "sulphite" (pp. 74 and 78) should be "sulphide" in a test for bismuth.

As a summary of the work done in this field, the book has a certain amount of interest and use for the specialist, but its value would have been enhanced had it included representative analyses for minerals, rocks, and marine deposits to which, it is stated, extensive application has been made in geochemical studies over many years. L. S. THEOBALD

PRACTICAL ANALYTICAL METHODS FOR CONNECTIVE TISSUE PROTEINS. By J. E. EASTOE and A. COURTS. Pp. xiv + 145. London: E. & F. N. Spon Ltd. 1963. Price 42s.

On reading the title to this book, one is apt to concentrate on the key word "protein" and to overlook the qualifying words "connective tissue," so that one is surprised when, on randomly opening the volume, one sees a chapter heading "The Analysis of Carbohydrate Sub-units." The surprise vanishes when one remembers that connective tissue proteins include those muco-proteins and glycoproteins that are protein - carbohydrate complexes.

As the title implies, this is essentially a book for the laboratory and it embodies the experience of the authors with the British Gelatine and Glue Research Association and may therefore be considered to be authoritative in its field. The first chapter deals with the preparation of collagen, gelatine and other constituents of connective tissue for analysis, *i.e.*, free from matter physically rather than chemically associated, such as apatite in bone, and enamel in teeth. This is followed by methods for the primary analysis of proteins—determination of ash, moisture, nitrogen and protein. Then comes the kernel of the problem in the determination of amino-acid composition, by the ion-exchange chromatographic method of Moore and Stein and the dinitrophenyl end group method of Sanger, both of which, though still relatively young, qualify for the designation "classic." These methods are supplemented by the description of thin-layer chromatographic methods directed to the same end. The final chemical aspects refer to the determination of carbohydrates, hexosamines, hexuronic and sialic acids in association with the various tissue proteins. A chapter on the physical properties of the macro-molecule deals with the iso-ionic point, viscosity, gel properties, spectral absorption and optical rotation.

Though the objective of the book is limited to the analytical problems of gelatine and glue research and control, it is a convenient source of practical detail for the broader field of protein and glycoprotein analysis, and as such, should find a place in many laboratories. J. I. M. JONES

QUANTITATIVE ORGANIC ANALYSIS VIA FUNCTIONAL GROUPS. By SIDNEY SIGGIA, Ph.D. Third Edition. Pp. xiv + 697. New York and London: John Wiley and Sons Ltd. 1963. Price 145s.

The preparation of the third edition of this standard text-book on the determination of organic functional groups by chemical procedures has involved considerable revision of the second edition, published nine years ago.

Many new methods have been added, and particular attention is now directed to the determination of trace amounts of functional groups. Analytical chemists concerned with the analysis of organic substances whether acids, esters, ketones, sulphoxides, sulphides, nitriles, amines, nitro compounds or almost any other type of compound will want to see this book on their shelves.

Some of these workers will prefer more old-fashioned titrimetric or colorimetric determinations of reaction products, whilst others will want to use instrumental methods whenever convenient. It does not really matter, however, because, in any case, the fundamental chemistry of a particular test will need to be correctly understood and this text-book will ensure that this is the case.

Each chapter is dealt with on rather similar lines, *e.g.*, in the chapter on unsaturation, attention is first paid to the chemistry of the various processes. Bromination methods, by using bromine in solvents, bromate - bromide solutions and electrolytically generated bromine are described in detail, and there is adequate discussion of the results obtained when the tests were applied to known substances. Similar considerations apply to the methods for determining the iodine number, to hydrogenation procedures and to methods involving the use of mercuric acetate.

Again and again in reading this book one is struck by the great increase in non-aqueous titrimetry, often with recorded potentiometric titration of the reaction products of a test.

Interesting developments are described, including, for example, the use of pyromellitic dianhydride for determining hydroxyl compounds and the titration of hydroxyl compounds, *e.g.*, 1-naphthol, in non-aqueous media with tetrabutylammonium hydroxide. Silver - amine complexes that may replace the older Tollen's reagent are described, and the novel use of morpholine for determining acid anhydrides merits attention. Some excellent methods are presented for determining non-ionic surfactants and epoxides, whereas analytical chemists interested in coulometric methods will be keen to know more of constant-current sources, accurate to 5 parts in 10,000.

The ability of a neutral salt to enhance the potentiometric titration of a weak base is discussed, and some interesting methods depending on differential reaction rates are presented.

There are plenty of omissions. One looks in vain for colorimetric methods for determining acetylenic hydrogen, for methods of direct instrumental titration of amines with nitrite, for Marshall's method of determination of unsaturation, for the colorimetric determination of tertiary amines in mixtures after acetylation of the primary and secondary amines, for full-scale conductimetric titrations and for the precise and simple method of location of the end-point in the many potentiometric titrations that are described.

Moreover, there are several errors in the book, some queer sentences and, on p. 427 it is even stated that the initial portions of two curves are "superimpossible."

These are minor blemishes, however, and there is no doubt that this book will be welcomed by very large numbers of analytical chemists with work to do on the laboratory bench.

JOHN HASLAM

PHYSICAL AND CHEMICAL METHODS OF SEPARATION. By EUGENE W. BERG, Ph.D. Pp. xiv + 366. New York, San Francisco, Toronto and London: McGraw-Hill Book Company Inc. 1963. Price 97s.

This is a useful book that gathers together in one volume a number of diversified methods of separation and discusses the principles on which they are based, points out their limitations and shortcomings and gives examples of their application. It would be an excellent reference text-book in any advanced level course on analysis, and should prove of interest to all chemists who require to obtain pure specimens of the components of mixtures. It should certainly be available in any self-respecting chemical library; its price is likely to exclude it from private bookshelves.

R. A. CHALMERS

VACUUM MICROBALANCE TECHNIQUES. Volume 3. Edited by KLAUS H. BEHRNDT. Pp. xvi 215. New York: Plenum Press Inc. 1963. Price $9.50.

This book represents the Proceedings of a Symposium held at Los Angeles in 1962, although the appearance of its dust jacket suggests a more comprehensive text. The field covered is so specialised that major advances naturally occur infrequently, and this is reflected in the fact that only one of thirteen papers describes a new approach to vacuum weighing. The majority of the papers are reports of the modification or operation of balances described in detail at previous Symposia or elsewhere. A number of papers, reporting work in which balances of established design were used, are relevant only as examples of their application, and should have been published elsewhere as appropriate.

In the papers by Poulis and Thomas, approximate treatments are given of the limitations to microbalance sensitivity set by Brownian motion and thermo-molecular effects. The arguments are well set out and easily followed. Methods are suggested by which both effects may be minimised in practice.

The papers by Mayer *et al.*, although somewhat fragmentary, illustrate well the application of torsion balances of simple design to elegant studies of surface phenomena in ultra high vacuum.

Simple torsion balances are not generally sufficiently sensitive to allow study of the submonolayer aspects of adsorption on metal films, and the development of more sensitive devices such as oscillating quartz crystal mass detectors is important. The paper by Warner and Stockbridge is thus particularly valuable, since a number of the problems associated with this type of instrument are discussed at greater length than would normally be possible in journal publication.

An interesting magnetic levitation coupling device, described by Gast, allows containers within a vacuum system to be weighed by an external balance.

N. J. Carrera *et al.* discuss the use of image-furnace techniques for obtaining sample temperatures in excess of 2000° C in connection with the use of a Gulbransen balance for studies of high temperature reactions. In view of the elaborate ultra high vacuum techniques employed, it was

somewhat surprising to find that their balance could not be baked above 300° C owing to the use of silver chloride cement.

Clear diagrams and large well-spaced type make the book easy to read, but bulkier than necessary.

D. W. BASSETT

RADIOACTIVATION ANALYSIS. By H. J. M. BOWEN and D. GIBBONS. Pp. vi + 295. Oxford: Clarendon Press: Oxford University Press. 1963. Price 50s.

Since the end of the Second World War there has been an explosive increase in the number of papers dealing with radioactivation analysis and its applications. The appearance of this volume by two members of the staff of the Wantage Research Laboratory of the Atomic Energy Research Establishment is therefore to be welcomed.

The earlier chapters of the book deal with general principles, including such matters as activation by neutrons and other particles, gamma scintillation spectrometry, determination of radioactivity, errors in activation analysis, separation of radionuclides and the preparation of sample material. Later chapters cover geochemical, biological and inorganic and pure chemical applications. A feature of the book is the inclusion, as a final chapter, of practical details for the analysis of 85 chemical elements.

The authors have succeeded in writing an authoritative and thoroughly readable book in which much of their personal experience is illustrated. The volume contains many clear original diagrams and several useful tables of data. It is also reasonably priced. However, there appears to have been a considerable delay between the writing and publication of the book. This leads to some criticisms. Thus it is misleading to read that accelerator sources of neutrons are not used a great deal, particularly if one considers the work of such investigators as Guinn, Anders and Coleman. It is also a pity that more could not have been included on the use of digital computers for correcting, normalising and resolving gamma-ray spectra. Finally, it must be mentioned that in a case where a radiochemical separation is required, an analyst is unlikely to embark on a procedure described in the final chapter of the book without first having consulted the appropriate monograph in the NAS–NS series, Radiochemistry of the Elements (see *Analyst*, 1961, **86**, 763).

D. F. C. MORRIS

BRITISH PHARMACOPOEIA 1963. Published under the Direction of the General Medical Council. Pp. xxviii + 1210. London: The Pharmaceutical Press. 1963. Price 100s.

The new (10th) edition of the British Pharmacopoeia reflects the rapidly increasing use of chemotherapy, providing specifications and methods of analysis for those substances in significant use in medicine and for the reagents involved. The monographs now approach 1,000 and include 211 new ones with 105 deleted.

The change from the imperial to the metric system for doses and for strengths of preparations is now completed, the imperial system being omitted from the monographs. To facilitate the change, the imperial doses and strengths directed to be the equivalent to the metric, are given in an appendix.

There is an increase in the use of physical methods for the analysis of substances: ultraviolet and infrared spectrometry, photometry, paper chromatography and potentiometric titrations. Newer techniques of chemical analysis, notably complexometric and non-aqueous titrations and the oxygen-flask method, are increasingly used.

It is interesting to note that in some instances (benzylpenicillin, benzathine penicillin and procaine penicillin) it has been possible to replace biological assay with chemical tests and assays.

There appears to be a tendency for substances of natural derivation to return, but in a different guise, those of vegetable origin further receding, but those derived from fermentation processes increasing.

Increase in the scope of standardisation is seen in the requirements for uniformity of weight of capsule contents.

Among changes noted are that the atomic weights used are those of the "Table of International Weights for 1955" based on the carbon-12 scale instead of atomic weight of oxygen of 16, the brief reference to authentic specimens for comparison of infrared spectra, a test for peroxides in vegetable oils, the use of silicone fluids for melting-point baths in place of sulphuric and nitric acids and a method for determination of the carbon dioxide absorption properties of soda-lime.

The volume indicates the wide range of medicine in the chemical field and the variety of analytical techniques that have had to be drawn upon.

H. E. BROOKES