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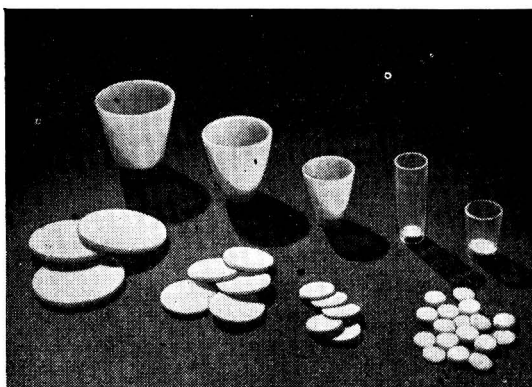
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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS
AND OTHER ANALYTICAL CHEMISTS

Report of the Analysts' Sub-Committee of the Ministry of Health Conference on the Differential Assay of Penicillin Part I

The Determination of Benzyl Penicillin by Precipitation with N-Ethylpiperidine

INTRODUCTION

At a meeting held at the Ministry of Health in December, 1946, under the chairmanship of Sir Weldon Dalrymple-Champneys, the importance of obtaining agreement on standard methods of determining the various penicillins was stressed. Accordingly, another meeting was convened on February 10th, 1947, by the Ministry of Health. This meeting, under the chairmanship of Dr. A. A. Miles of the National Institute for Medical Research, was attended by representatives of the various manufacturers of penicillin, the Ministry of Supply, the Ministry of Health and the National Institute for Medical Research, and was known as the "Conference on the Differential Assay of Penicillin." The practicability of the methods of differential assay was discussed in the light of recent experience and it was decided to examine further the N-ethylpiperidine precipitation method for the determination of benzyl penicillin. The results obtained by members of the Conference, after examination of some twelve samples of penicillin by their own interpretations of the method, showed such wide variation that, at a meeting of the Conference held on June 17th, 1947, it was decided to appoint a sub-committee of analysts from the four manufacturing firms and the Ministry of Supply (Chemical Inspectorate), with the specific assignments of (1) examining and assessing the validity of the N-ethylpiperidine precipitation method, with a view to standardising and improving it if possible, so as to render it a suitable method for the determination of benzyl penicillin in samples of penicillin containing approximately 90 per cent. or more of benzyl penicillin and (2) setting up and evaluating a working standard penicillin containing approximately 90 per cent. of benzyl penicillin and 10 per cent. of other penicillins. The evaluation of this standard was to be made by comparison with a purified sample of crystalline benzyl penicillin containing 98 to 99 per cent. of benzyl penicillin (subsequently referred to as the "A.S.C. Standard"), which was in turn to be compared with the purest sample of benzyl penicillin available to the Conference (subsequently referred to as the "M.U. Standard" or Manufacturers Ultimate Standard). With the increasing purity of commercial penicillin it had become difficult to obtain from ordinary stocks samples containing only 90 per cent. of the benzyl compound; it was decided, therefore, at later meetings of the Conference that a salt containing a higher proportion of benzyl penicillin would be acceptable as a working standard.

The Sub-Committee appointed was as follows—

- C. R. Bond, M.Sc., F.R.I.C., Imperial Chemical Industries Ltd., (*Chairman*).
 L. J. Bellamy, B.Sc., Ph.D., Ministry of Supply
 A. R. Graham, Ph.D., A.R.I.C., Distillers Company Ltd. (from October, 1947)
 T. Henshall, M.A., D.Phil., Distillers Company Ltd. (until October, 1947)
 T. E. V. Horsley, B.Sc., F.R.I.C., Glaxo Laboratories Ltd.
 G. F. Hall, M.B.E., B.Sc., F.R.I.C., Boots Pure Drug Co. Ltd., (*Hon. Secretary*).

and, at some meetings, it has been pleased to receive the assistance of

- P. D. Coppock, M.Sc., F.R.I.C., Distillers Company Ltd.
 A. F. Lerrigo, B.Sc., F.R.I.C., Glaxo Laboratories Ltd.
 M. E. D. Windridge, M.A., B.Sc., F.R.I.C., Robinson Bros. Ltd.

The method under consideration was proposed by Sheehan, Mader and Cram¹ and was subsequently adopted, with modifications, by the Food and Drug Administration of the United States. It consisted, briefly, of extraction of an acidified aqueous solution of the penicillin salt with amyl acetate and subsequent precipitation of the N-ethylpiperidinium salt from a mixture of amyl acetate and acetone. The Sub-Committee, after consideration of the various modifications in use, agreed upon the following procedure.

METHOD

REAGENTS—

In the course of the investigation it became apparent that, to obtain satisfactory results, the reagents must be of a high standard of purity. In particular, the use of highly purified N-ethylpiperidine is essential. It is hoped that, as a result of discussion with the manufacturers, a suitable grade of N-ethylpiperidine will be generally available.

Special Note—All reagents shall be cooled in an ice water bath before use.

I. *Acetone solution*—Acetone (A.R.), containing not more than 0.3 per cent. of water, saturated with the N-ethylpiperidinium salt of benzyl penicillin at room temperature, cooled in ice-water and gravity-filtered.

The water content of the acetone is determined by the method of Smith and Bryant² modified as follows: (a) The solution is left with occasional swirling for at least 10 minutes after the addition of the first portion of absolute alcohol. (b) α -Naphtholphthalein is used as the indicator. The best end-point is obtained by adding a small excess of alkali and titrating back with 0.2 N acid after addition of fresh indicator.

II. *Amyl acetate solution*—Amyl acetate (A.R.) saturated with the N-ethylpiperidinium salt of benzyl penicillin at room temperature, cooled in ice-water and gravity-filtered.

III. *Acetone - amyl acetate solution*—A mixture of equal volumes of acetone and amyl acetate, both of the standard of purity described above, saturated with the N-ethylpiperidinium salt of benzyl penicillin at room temperature, cooled in ice-water and gravity-filtered.

IV. *Phosphoric acid solution*—2 ml. of phosphoric acid B.P., diluted to 10 ml. with distilled water.

V. *N-ethylpiperidine solution*—2 ml. of N-ethylpiperidine diluted with 8 ml. of amyl acetate (A.R.), saturated with the N-ethylpiperidinium salt of benzyl penicillin at room temperature, cooled in ice-water and gravity-filtered.

The N-ethylpiperidine used shall comply with the following specification.

Purity (from alkalinity to bromophenol blue):	99.5 to 100.5 per cent.
Boiling range:	95 per cent. shall distil between 129.5° and 131.5° C. and the distillation shall be complete at this temperature.
Refractive index (20° C.):	1.4438 to 1.4440.
Specific gravity	
(15.5°/15.5° C.):	0.827 to 0.829.
(20°/20° C.):	0.825 to 0.827.
Storage test:	Store under air in diffused daylight at 20° C. for 3 days; no change in colour and no precipitation shall occur.

- Carbon disulphide test: Mix 0.5 ml. of the sample with 5 ml. of light petroleum (50° to 60° C.). The solution shall be clear and colourless. On the further addition of 1 ml. of carbon disulphide the solution shall be clear and colourless.
- Test for piperidine: It shall contain not more than 0.4 per cent. of piperidine when tested by the following method. Transfer 1 ml. to a test tube and add, shaking vigorously after each addition, 1 ml. of freshly distilled carbon disulphide, 5 ml. of 20 per cent. w/v copper sulphate solution, 10 ml. of chloroform and, from a burette, 25 per cent. v/v sulphuric acid drop by drop until the blue-green gelatinous precipitate has redissolved and both layers are clear. Compare the colour of the lower layer by transmitted light with that of blank tests carried out in precisely the same manner, in which 0.2 ml., 0.4 ml., 0.6 ml., 0.8 ml. and 1.0 ml. respectively of 0.5 per cent. w/v aqueous piperidine solution are taken in place of the N-ethylpiperidine.
- Appearance: It shall be free from turbidity and shall be practically colourless. Samples not complying with this requirement shall be redistilled.

VI. *Sodium sulphate*—Powdered anhydrous sodium sulphate (A.R.) that has been freshly ignited.

PROCEDURE—

Special Note—After the initial weighing of the sample it is essential that all operations shall be carried out under ice-cold conditions.

From a suitable stoppered weighing bottle (Note 1) weigh accurately, by difference, about 120 mg. of the sample (Note 2), into a 15-ml. centrifuge tube. Add 5 ml. of water and dissolve. Stand the tube in ice-cold water and allow to cool. Add 5 ml., accurately measured, of amyl acetate solution (Reagent II) and 0.5 ml. of phosphoric acid solution (Reagent IV); stopper with a wet cork and shake immediately for 15 seconds. Centrifuge for 30 seconds. Pipette off the aqueous layer completely, add to the centrifuge tube 0.5 g. of sodium sulphate (Reagent VI), stir, allow to stand for 5 minutes in ice-cold water and then centrifuge for 30 seconds. Replace in ice-cold water for 5 minutes, pipette off a 3-ml. aliquot into a suitable tared centrifuge tube (Note 3) containing a thin glass rod slightly curved at the end. Add 3 ml. of acetone solution (Reagent I) and 1.5 ml. of N-ethylpiperidine solution (Reagent V); stir, close the mouth of the tube with a rubber thimble, place the tube inside a test tube, close the test tube with a cork and stand it in ice-cold water for 2 hours (Note 4). Remove the centrifuge tube and centrifuge for 1 minute. Break the surface to dislodge any particles at or above the surface of the liquid and again centrifuge for 1 minute. Decant off the supernatant liquor and wash the precipitate by stirring with 2 ml. of acetone - amyl acetate solution (Reagent III) followed by centrifugation for 1½ minutes and decantation. Wash twice by stirring with 2 ml. of ether (Note 5) followed by centrifugation for 1½ minutes and decantation. Smear the deposit over the inside of the tube by means of the curved glass rod and dry at room temperature *in vacuo* to constant weight, the tube being placed in a nearly horizontal position.

$$\text{Per cent. sodium benzyl penicillin by weight} = \frac{\text{weight of precipitate}}{\text{weight taken}} \times 132.8$$

N.B.—The determination of total penicillins, which is required for the expression of results as a percentage on total penicillins, should be made by the iodimetric procedure described in Part II of this Report.

Notes—

(1) A weighing bottle of small diameter is advisable. Its weight should be not more than 15 g.

(2) With 100,000-unit packed bottles, freeze-dried *in situ*, the contents of two bottles should be taken as completely as possible.

(3) The total weight of the centrifuge tube and the glass rod should be not more than 15 g.

(4) A standing time of 2 hours was adopted since higher recovery and greater uniformity of results were thereby obtained than at $\frac{1}{2}$ or 16 hours.

(5) As the solubility of the precipitate, especially in acetone, is considerably influenced by rise of temperature, it was decided to adopt the washing procedure detailed above.

The main difficulty confronting the Sub-Committee in its work was the determination of the absolute recovery by the method in the absence of a sample of benzyl penicillin the purity of which could be proved by any known means. It was therefore decided to accept the M.U. Standard as 100 per cent. sodium benzyl penicillin, because available methods did not indicate measurable amounts of impurities in it and it was the most highly purified sample of benzyl penicillin examined by the collaborators.

The results of determinations on the M.U. and A.S.C. Standards are given below; micro-chromatograms⁹ and infra-red spectra were examined and the potency was determined by repeated microbiological assay. The various results by individual workers were in close agreement.

M.U. STANDARD

Other penicillins—

X (by micro-chromatogram)	trace;	(by infra red spectra)	} Not detectable within limits of accuracy of method (less than 2 per cent.)
F " "	nil ;	" " " "	
D " "	nil ;	" " " "	
K " "	nil ;	" " " "	

Potency (biological assay): 1710 units/mg. (± 60 units)
(British National Standard \equiv 1600 units/mg.).

Sodium benzyl penicillin by method described:	Member A	98.2 per cent.
	" A	98.6 "
	" B	99.0 "
	" B	99.0 "
	" B	98.8 "
	" B	98.4 "

A.S.C. STANDARD

Other penicillins—

X (by micro-chromatogram)	< 0.1%;	(by infra red spectra)	} Not detectable within limits of accuracy of method (less than 2 per cent.)
F " "	ca. 0.3%;	" " " "	
D " "	\leq 0.1%;	" " " "	
K " "	\leq 0.1%;	" " " "	

Potency (biological assay) (mean figures): Member A 1643 units/mg.
(British National Standard \equiv 1600 units/mg.)

	" B	1681 "
	" C	1678 "
	" D	1636 "
	" E	1683 "
Sodium benzyl penicillin by method described (mean figures):	Member A	95.4 per cent.
	" B	96.9 "
	" C	95.0 "
	" D	96.2 "
	" E	96.6 "

Grand mean: 96.1 " (S.E. 0.19)

Assuming the purity of the M.U. Standard to be 100 per cent., the Sub-Committee is of the opinion that, at this level, a 98.6 per cent. recovery figure is obtained. Accordingly, as the (weighted) mean assay result for the A.S.C. Standard is 96.1 per cent., after correction on a 98.6 per cent. recovery basis, it has been assigned a sodium benzyl penicillin content of 97.5 per cent.

In order to examine further the reproducibility of the method, determinations were also made on an N-ethylpiperidinium salt of penicillin; the following results were obtained—

N-ETHYLPIPERIDINIUM SALT OF PENICILLIN

Benzyl penicillin by method described	Member A	97.5 per cent.
(calculated as N-ethylpiperidinium	” B	96.6 ”
benzyl penicillin) (mean figures):	” C	95.3 ”
	” D	95.7 ”
	” E	97.5 ”

Grand mean: 96.5 per cent.

Statistical examination of the individual determinations on this sample, which were heavily weighted by twenty-six determinations by member C, showed the weighted mean to be 96.1 per cent. (S.E. = 0.16) and also showed that the differences between laboratories were significant.

In order to complete the work on the examination of the validity of the proposed method the composition of a range of samples was determined by employing iodimetric assay to determine the approximate amount of inert matter, and micro-chromatographic assay to determine what proportion of the penicillins was benzyl penicillin. The composition of the N-ethylpiperidine precipitates was also examined micro-chromatographically, so as to determine to what extent co-precipitation with other penicillins was taking place, and iodimetrically to determine the amount of inert material in the precipitate (Table I).

In all these micro-chromatographic examinations the method of calculation given by Goodall and Levi³ was employed, using, where available, more up-to-date figures for the *B. subtilis* potencies of the various penicillins in the conversion from percentage composition in *B. subtilis* units to percentage composition by weight. In view of the considerable error to which the micro-chromatographic method is subject it must be borne in mind that all the values quoted for the composition of samples and precipitates can only be approximate.

One of these samples (PPD/AS/0239—an N-ethylpiperidinium salt) had a composition approximating more nearly than any other available sample to the limiting level of 90 per cent. benzyl penicillin at which it was proposed to use the method. This was examined in more detail than the other samples with the results shown below.

SAMPLE PPD/AS/0239

Benzyl penicillin determined by the	Member A	93.1 per cent.
method described (calculated as N-	” B	92.8 ”
ethylpiperidinium benzyl penicillin)	” C	92.6 ”
(mean figures):	” D	91.8 ”
	” E	93.5 ”

Grand mean: 92.7 ” (S.E. 0.36)

The differences between laboratories were not significant.

Proportions of penicillins in the sample and in its N-ethylpiperidinium precipitate, by micro-chromatographic analysis.

Penicillin	Laboratory B		Laboratory C	
	Sample	Precipitate	Sample	Precipitate
X.	0.1	0.1	0.1	0.1
U ₁	0.5	0.5	0.3	0.4
G	93.3	93.6	96.1	97.4
F	2.9	2.4	1.3	1.3
D	2.3	2.3	1.3	0.8
K	1.1	1.0	0.8	—
No. of determinations:	4	2	4	3
G range:	92.2	93.4	95.9	96.4
	to	to	to	to
	93.9	93.7	96.4	98.3
Potency (<i>S. aureus</i>) u./mg.	1342	—	1340	1370

TABLE I

Sample	Potency <i>S. aureus</i> units (a)	Penicillin % (iodim.) w/w (b)	Benzyl penicillin as % of total penicillins (micro- chromatogram) <i>B. subt.</i> units (c)		Benzyl penicillin % in sample (b) × (d) 100 (e)	Benzyl penicillin by pptn. % (un- corrected) (f)	Benzyl penicillin as % on total penicillins in precipitate (micro- chromatogram) <i>B. subt.</i> units (g)		Penicillin in pre- cipitate (iodim.) % w/w (of theoretical) (i)
			w/w (d)	w/w (h)					
M.U. Standard	1710	100	99.9	99.9	99.9	98.6	99.9	99.9	—
A.S.C. Standard	1664	98.5	99.7	99.5	98.0	96.1	98.8	97.6	100.2
48/0239 ..	1340	100	96	93	93	92.8	97	94	—
48/0058 ..	1490	87	72	56	49	47.1	90	83	99.2
365 ..	660	37.7	81	69	26	13.3	93	88	87.0
48/0372 ..	—	95.7	93	83	84	81.9	96	92	99.9
48/0373 ..	—	95.3	92	86	82	83.0	94	90	99.8
2269/29/3	—	100	9	5	5	0.0	—	—	—

Note (1). Sample 48/0239 is an N-ethylpiperidinium salt, and figures under (b) and (f) are calculated accordingly.

Note (2). Sample 2269/29/3 was a synthetic mixture of penicillin sodium salts virtually free from inactive impurities composed as follows.

Penicillin X	0.2 per cent. w/w	Penicillin F	31.2 per cent. w/w
" U ₁	0.2	" D	45.5
" G	4.7	" K	18.0

Note (3). As a basis for calculation of the iodimetric figures, a mean molecular weight of 356 (*i.e.*, the molecular weight of sodium benzyl penicillin) has been used throughout. With penicillin containing 90 per cent. of G or over, with which this work is primarily concerned, the errors thereby introduced are slight; even if the sample contained 90 per cent. of G and 10 per cent. of F, where the maximum error would be met, the G figure would be incorrect only to the extent of 0.66 per cent.

Note (4). As a basis for calculation, the following conversion factors (*B. subtilis* units) for the individual penicillins were used.

X	1500	Schmidt, Ward and Coghill ⁴
U ₁	1500	Assumed—no data available—traces only present
G	1667	By definition
F	970	Schmidt, Ward and Coghill ⁴
D	660	Determined on pure specimens prepared by T. Leigh (I.C.I.). (National British Standard ≡ 1600 u./mg.)
K	845	

Note (5). The nomenclature used for the various penicillins in the order of the zones on the chromatographic strip is as follows.

Penicillin X	<i>p</i> -Hydroxybenzyl penicillin
" U ₁	—
" G	Benzyl penicillin
" F	Pent-2-enyl penicillin
" D	<i>n</i> -Amyl penicillin
" U ₂	—
" U ₃	—
" U ₄	—
" K	<i>n</i> -Heptyl penicillin
" U ₅	—

A study of the results given in these tables shows that the precipitation procedure gives a precipitate which, except with the already pure M.U. Standard, is not composed of the N-ethylpiperidinium salt of pure benzyl penicillin (compare (c) with (g) and (d) with (h) in Table I). It is shown however in Table I that, in the range 90 to 100 per cent. benzyl penicillin, there is some agreement between the calculated benzyl penicillin content of the samples examined and the amount determined by the proposed method. It may well be, therefore, that there is, in fact, a compensation of errors in this range.

The standard deviation of some thirty determinations on the A.S.C. Standard and thirty-one determinations on the N-ethylpiperidinium salt was 1.24 per cent.

In view of these findings the Sub-Committee recommends that the procedure described be used as a tentative method in the examination of samples of penicillin consisting substantially of benzyl penicillin. In consideration of the appreciable error to which the proposed method is subject and its susceptibility to slight variations in the quality of the reagents used, to temperature, etc., and inasmuch as the differences in the results on the same sample between laboratories were sometimes significant, the Sub-Committee considers it is desirable that a standard penicillin should be assayed alongside the test sample and a correction applied equal to the difference between the benzyl penicillin content found for this standard and its actual value. For reference purposes the Sub-Committee, with the approval of the Ministry of Health, has standardised a quantity of sodium benzyl penicillin, designated the "Benzyl Penicillin Gravimetric Standard," to which a value of 95.8 per cent. sodium benzyl penicillin has been assigned.

The Sub-Committee is indebted to all those who have assisted in the experimental work, to Imperial Chemical Industries Ltd., for providing the M.U. and A.S.C. Standards, to the Distillers Company Ltd. for providing the sample of N-ethylpiperidinium salt, to Mr. Primavesi of the Distillers Company for his modification of the Smith and Bryant method, to Robinson Bros. Ltd. for their gift of N-ethylpiperidine and to Mr. Windridge for permission to include the details of the test for piperidine.

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January, 1949

Ether Peroxide as a possible Source of Error in the Röse - Gottlieb Butter-Fat Test

BY M. M. MUERS AND MISS M. A. HOUSE

(Read at the meeting of the Society on Wednesday, October 6th, 1948)

IN the course of control work in the manufacture of evaporated milk, it was observed that the figures for fat reported by a country creamery control laboratory were nearly always slightly higher than the Central Laboratory figures for the duplicate samples. Both laboratories used the Mojonnier method, and each obtained agreement to within 0.05 per cent. of fat between its own duplicate tests, but the differences between the means for the two laboratories ranged from 0.02 to 0.19 on a fat figure of 9 per cent. The blank for both sets of reagents was negligible, but the use of creamery reagents at the Central Laboratory confirmed local results. Subsequently, similar differences were found for two other creameries.

Ethyl ether, used in the analysis, is known to form peroxide and it seemed possible that this might react with butter fat and thereby increase its weight. Such an effect has been found by Middleton¹ with oleic acid; and, since this work was started, a similar suggestion has been put forward by Janse,² but without any experimental evidence. As samples of the ether used at the three creameries all gave strong peroxide reactions, the above suggestion was tested, with the results shown in Table I.

TABLE I

FAT IN EVAPORATED MILK, MOJONNIER METHOD

Ether from	Other solvents from	Laboratory	Fat found per cent.
Creamery (peroxide-positive) Creamery	Creamery	9.39, 9.38
" " " " "	Central	9.41, 9.41
Central Laboratory (peroxide-negative)	.. "	"	9.31, 9.32
" " " " Central Laboratory	"	9.34, 9.36

In analyses by the Röse - Gottlieb and Werner - Schmid methods similar or larger differences were encountered. Also, when mixtures of a known weight of pure butter-fat with specially purified solvents, in the proportions used for the Röse - Gottlieb analysis, were evaporated and heated to constant weight in the usual manner, the following results were obtained (means of duplicates).

TABLE II

Control (no solvents)	99.48% recovery
All pure solvents	99.76% "
Peroxide-positive ether, other solvents pure	100.8% "

These results show that the major part of the effect is in fact due to ether containing peroxide.

Owing to the supply position in war-time, large stocks had been held at the country laboratories, where some of the ether was several years old, whilst Central Laboratory ether was fresh and peroxide-free. Peroxide estimations on the old ether by the method of Nozaki³ gave amounts of active oxygen up to 0.08 per cent., and if this all combined with the fat it would be ample to account for the observed differences.

In order to prevent the discrepancies and possible risk of explosion which may arise from use of peroxidised ether, it was desired to treat it in such a way that peroxide would be removed and prevented from reappearing under normal laboratory conditions. For use in factory laboratories, a simple method which would avoid such operations as distillation or filtration of large volumes of ether was necessary. Additions of small amounts of many antioxidants have been suggested in the literature, *e.g.*, diphenylamine, β -naphthol or hydroquinone. Of those tried, only diphenylamine had any effect, but it was unsuitable because it caused rapid discoloration. The use of various metals has also been reported, but Bailey and Roy,⁴ using ether dried over sodium, found that only sodium amalgam was really effective in preventing peroxide formation in daylight. It has now been found that many metallic couples, especially zinc - copper, magnesium - copper, iron - tin and aluminium - mercury completely remove peroxide from *moist* ether and prevent its re-formation even in bright daylight. The presence of a little water is necessary except with aluminium - mercury, which has a slow action even in dried ether. Fifty-ml. lots of peroxidised ether, dried over anhydrous calcium sulphate to a water content (Karl Fischer titration) of 0.01 per cent., were treated with 100 sq. cm. of metal surface, alone and in presence of 2 per cent. of added water, and titrated at intervals as shown in Table III.

TABLE III

REMOVAL OF PEROXIDE FROM ETHER BY VARIOUS COUPLES

The figures represent ml. of 0.02 N thiosulphate per 5 ml. of ether

Duration of treatment	Al - Hg	Fe - Cu	Fe - Sn	Mg - Cu	Zn - Cu	Control
Without added water:						
Days 0	—	—	—	—	—	13.6
" 1	2.8	12.6	12.5	12.6	12.8	13.6
" 5	1.8	11.6	13.2	12.7	13.0	13.6
With 2% of added water:						
Days 0	—	—	—	—	—	13.5
" 1	0.0	0.2	0.5	0.4	0.3	13.9
" 2	—	—	0.1	0.2	0.0	—
" 5	0.0	0.0	0.0	0.0	0.0	14.2

The reaction is evidently a reduction of peroxide with formation of metal hydroxide. Aluminium and magnesium couples cause an inconvenient effervescence in moist ether. For treatment of ether intended for fat determinations, we prefer a zinc - copper couple prepared by immersing zinc foil in acidified copper sulphate solution for about a minute, washing, and transferring it while still wet to the ether container. Satisfactory results have been obtained in 5-gallon cans, using seven or eight 50- × 5-cm. strips of the treated zinc foil. The zinc hydroxide formed is dissolved both by the ammonia used in the Röse - Gottlieb and by the hydrochloric acid used in the Werner - Schmid method, and therefore the treated ether need not be filtered. Such ether gives a negative test for peroxide with titanous acid reagent, and gives results for fat analyses agreeing very closely with those obtained with pure re-distilled ether, as shown by the examples cited in Table IV.

TABLE IV

FAT ESTIMATIONS IN MILK PRODUCTS

The figures are means of duplicates

	Pure ether %	Peroxide-positive ether %	Treated ether %
Evap. milk, Röse - Gottlieb	9.28	9.48	9.34
" " " "	9.03	9.09	9.01
Butter-fat " "	100.4	101.0	100.3
Milk powder, Werner - Schmid ..	26.66	26.97	26.70

Further investigation of the reaction between butter-fat and ether peroxide has provided some information on the fate of the peroxide oxygen. Pure butter-fat was treated by the procedure for a normal Röse - Gottlieb fat estimation, using purified reagents, except for peroxidised ether, and the amount of peroxide was determined at each stage. It was found that 13 per cent. of the original peroxide was washed out into the aqueous phase during the extraction stage, and 5 per cent. passed over into the distillate during evaporation of the solvents. The residual vapour and solvent in the flask, removed as usual at this stage by a gentle and brief current of air, was highly peroxidic, accounting for 77 per cent. of the total. The 5 per cent. of the peroxide remaining in the fat fell to 4 per cent. after heating to constant weight. Since the amount of active oxygen in this 5 per cent. would, by itself, account for an increase in weight of only 0.4 per cent., compared with up to 2 per cent. found in fat analyses, it seems that some other constituent of the peroxidised ether must be involved. Possibly the whole of the ether peroxide molecule combines with or is retained by the fat. The increase in weight of pure butter-fat treated with peroxidised ether alone was roughly proportional to the amount of peroxide present, and did not seem to depend on the amount of fat. Peroxidised ether itself left no weighable residue on heating, but when large amounts of peroxide were present with the fat, the latter took very long, up to 6 hours, to reach constant weight. This suggested that part of the weight increase might be due to a loose association, or possibly to a purely physical effect of the fat in delaying evaporation of some less volatile constituent of the ether. This theory was supported by the fact that the peroxidic distillate from a fat determination, when added to a further sample of fat, again caused a weight increase, though less than in the first determination. Moreover, purified B.P. paraffin, which would not be expected to react chemically with peroxide, showed a small increase in weight when treated with peroxidised ether. The destruction of the yellow colour of butter-fat, presumably by oxidation, during evaporation with ether peroxide, could not account for the weight increase because this was unaffected by preliminary removal of the colouring matter with charcoal.

It has been reported by Rieche^{5,6} that "ether peroxide" contains chiefly a polymeric ethylidene peroxide $(\text{CH}_3\text{CH} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array})_x$. A small quantity of this substance was prepared by

his method, but without isolating the intermediate or final products from ether solution, in order to minimise risk of explosion. The product, diluted with pure ether to a peroxide content comparable with that of stored ether, had properties qualitatively similar to the latter in nearly all respects, but it was less volatile in solvent vapour and caused a much larger (5 per cent.) increase in weight of butter-fat. The intermediate product, hydroxyethyl hydroperoxide, and also ethereal hydrogen peroxide (both of which were probable impurities in our preparation), caused no increase in weight. Treatment of the ethylidene peroxide solution with a zinc - copper couple removed all peroxide and eliminated nearly all the weight increase effect. Although not conclusive, this evidence does indicate that part of the material estimated as peroxide in stored ether is, in fact, Rieche's substance, and causes the weight increase, whilst the bulk of the peroxide is the less reactive part which passes over with the solvent vapour in a fat determination.

SUMMARY—

1. In butter-fat analyses by the Mojonier, Röse - Gottlieb and Werner - Schmid methods, the use of ether containing peroxide gives values that are too high by amounts up to 2 per cent. of the fat figure.

2. Peroxide can be removed, and prevented from re-forming, and correct fat values can be obtained, by treating such ether with metallic couples in presence of moisture. Zinc-copper couple is preferred, as the zinc hydroxide formed does not interfere with the analysis.

3. In a fat estimation most of the peroxide present is driven off with the solvents. The active oxygen left in the fat residue is insufficient to account by itself for the observed increase in weight of the fat.

4. The effect is roughly proportional to the amount of peroxide present.

5. Even pure B.P. paraffin shows a slight increase in weight when treated with peroxidised ether, although the latter alone leaves no non-volatile residue.

6. An ethereal solution of ethylidene peroxide has most of the properties of "ether peroxide," except that it causes a much larger increase in weight.

7. The results indicate that ethylidene peroxide is probably the constituent of "ether peroxide" chiefly responsible for the weight increase effect, but that some other component besides the active oxygen must be retained by the fat.

Our thanks are due to the Directors of United Dairies Limited, for permission to publish this paper.

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UNITED DAIRIES LIMITED
CENTRAL LABORATORY
WOOD LANE, LONDON, W.12

April, 1948

DISCUSSION

The PRESIDENT asked if there was any danger of an explosion with 0.08 per cent. of active oxygen in the ether and, if not, at what concentration the danger point was reached.

Dr. K. A. WILLIAMS said that explosions had occurred in the removal of ether from solutions of oxidised and polymerised oil eluted from chromatographic columns of alumina, and that these explosions had caused some damage. It was found that they were due to the use of ether that had been stored for some time, and it might well be that the danger of explosion was enhanced by the presence of the oxidised oil. He had for many years made it a practice in his own laboratory never to use ether without first distilling it from solid caustic soda. This method of purification seemed to remove peroxides satisfactorily, and, when it was used, he had never had any difficulty from them.

Dr. E. C. WOOD said that although distillation from caustic soda removed the peroxide it did not prevent its re-formation, as did the authors' method of adding a strip of zinc-copper couple to the stock bottle.

Mr. J. M. JONES asked if any work had been done with other ethers. *iso*Propyl ether seemed to form peroxides more readily than diethyl ether; moreover, the distillation residues from *isopropyl* ether exploded more regularly than did those from diethyl ether.

Mr. A. L. BACHARACH asked whether the recorded increases in weight of butter-fat might not be the result of atmospheric oxidation catalysed by peroxidised constituents of the ether. If so, one would expect the increases to exceed the unaccounted-for portion of the ethereal peroxides.

Mr. C. B. CASSON said that in his experience the fat extracted by peroxidised ether was not completely soluble in light petroleum, which suggested that polymerisation had taken place. He had found that the increased weight of the fat could be prevented by washing the extract with an acid sulphite solution before evaporation.

Mr. N. HERON said that the suggestion made by Mr. Bacharach that the oxidation of the oil is catalytic was probably true. The nature of the oil or fat has an effect on the extent of the reaction. Recently, during the determination of linseed oil in paints, an explosion occurred just at the end of the distillation of the ether. The ether used was from a general laboratory stock and no similar trouble was experienced in the extraction of fats of a more saturated nature, *e.g.*, milk-fat or beef stearin.

He had also observed other abnormal oxidations of vegetable oils. Sunflower seed oil, after drying at 100° C. yielded a large amount of material insoluble in light petroleum. The total ether extract of a sample recently examined was 12 per cent., but only 8 per cent. was soluble in petrol. The residue was also insoluble in methylated ether.

Dr. MUERS, in reply, said that from the literature it is certain that quite small amounts of peroxide may cause explosion, but for some very fortunate reason (possibly the presence of butter-fat), there have been no explosions during this work, even when deliberate attempts were made to produce one, on a small scale, by heat or shock.

Distillation over sodium hydroxide is one of many known methods for removing ether peroxide, but such methods are unsuitable for use with large volumes of ether by inexperienced workers in a factory laboratory. The authors' method is preferable because it is safe and simple. The treated ether gave negative tests for peroxide with vanadic acid, titanac acid, and potassium iodide - acetic acid reagents. No work has been done with *isopropyl* ether.

It is possible that part of the weight increase under discussion is due to atmospheric oxidation of the fat in the oven. The small amount of peroxide in the residue may be the remains of the ether peroxide left after evaporation, or fresh peroxide formed during heating. But the residue does reach a minimum weight during heating, and this stage is delayed when highly peroxidised ether is used, which is the reverse of what would be expected if peroxide catalysed fat oxidation.

The heated butter-fat residue from an extraction with peroxidised ether is quite soluble in light petroleum. In fact, in a fat determination the final net weight of fat is found by dissolving out the residue with petroleum ether and re-weighing the dry empty flask; but drying oils would no doubt behave differently.

Quantitative Photometric Determination of Diphenyl in Orange Peel

BY A. P. STEYN AND F. ROSSELET

EXTENDED use of wrappers impregnated with diphenyl for preserving citrus fruits has necessitated a search for an analytical method of sufficient sensitivity to assay the diphenyl absorbed by the fruit from the wrappers. The colorimetric method used by Tomkins and Isherwood¹ lacks sensitivity and, in consequence, Cox² suggested a photometric method based on the absorption characteristics of diphenyl dissolved in *cyclohexane*. Cox, however, did not develop the method for the problem under discussion. The results presented in this paper describe the development of an absorptiophotometric method of determining diphenyl in the micro-quantities present in citrus fruits that have been preserved by diphenyl-impregnated wrappers.

To indicate the quantities involved it may be mentioned that a medium-sized orange weighing 200 g. requires a wrapper 10 × 10 inches. Such a wrapper impregnated at the rate of 40 mg. per 100 square inches would contain 40 mg. of diphenyl. The greater part of the diphenyl absorbed by the fruit is found in the peel of the orange, so the maximum proportion that would normally be expected in the peel of a medium-sized orange is of the order of 650 p.p.m. Owing to losses of diphenyl by volatilisation to the air, the maximum concentration indicated above is seldom attained in practice. In order to correlate diphenyl content and preservative action the analytical method should be able to determine 0.2 p.p.m. of diphenyl with an accuracy to within 5 per cent.

ABSORPTION CHARACTERISTICS OF DIPHENYL—

Since diphenyl has a well-marked absorption band in the ultra-violet, this affords a simple and accurate method for its estimation.² According to Cox, diphenyl in *cyclohexane* shows an absorption maximum at 251 $m\mu$. having an $E_{1\%}^{1\text{cm}}$ value of 1200. A solution containing 0.001 per cent. of diphenyl will give a convenient reading in a 1-cm. cell.

The absorption curve of 20 p.p.m. of diphenyl in *cyclohexane* determined within the range 230 to 400 $m\mu$. is presented in Fig. 1. Diphenyl shows maximum absorption at 247 $m\mu$. with an $E_{1\%}^{1\text{cm}}$ value of approximately 1100. These differences in peak and extinction values from those obtained by Cox may be due to the respective purity of the samples of diphenyl used, or to changes in the optical system.

The purity of the diphenyl (B.D.H. brand) used in this laboratory was compared with spectrochemically pure diphenyl (Merck's brand). Both have absorption peaks at the same wavelength and the same $E_{1\%}^{1\text{cm}}$ value. To eliminate the optical factor, density readings are taken not at 247 $m\mu$., but at 250 $m\mu$., because the density is constant between 249 and 251 $m\mu$.

Spectrochemically pure chloroform cannot be used as a solvent,^{1,2} because it absorbs light at and below 250 $m\mu$. Spectrochemically pure *cyclohexane* is the most suitable solvent since (a) the solubility of diphenyl as well as orange oil in *cyclohexane* is high, and (b) *cyclohexane* does not absorb light at and below 250 $m\mu$. The method for the purification of *cyclohexane* is based on work done by Allsopp and Twyman.³

In the absence of a spectrophotometer and as a first approach, the absorption characteristics of standard solutions of diphenyl in spectrochemically pure *cyclohexane* ranging in concentration between 0.6 and 20 p.p.m. were determined on a Hilger medium quartz spectrograph, using nickel electrodes and a 1-cm. cell. The variations in the logarithm of the relative intensity of the line Ni 2501 recorded on an A.R.L. comparator-densitometer are plotted in Fig. 2 against the logarithms of the concentrations and give a straight line relationship. The accuracy is, however, only to within about 10 per cent. and is not considered sufficiently sensitive.

Through the courtesy of the University of Cape Town, the use of a Beckman quartz spectrophotometer, Model DU, as described by Cary and Beckman,⁴ was made available. The spectrophotometer is more accurate and more convenient than the spectrograph for absorption work and the mean percentage error of the determination of diphenyl in the standard solutions was of the order of 2.2 per cent.

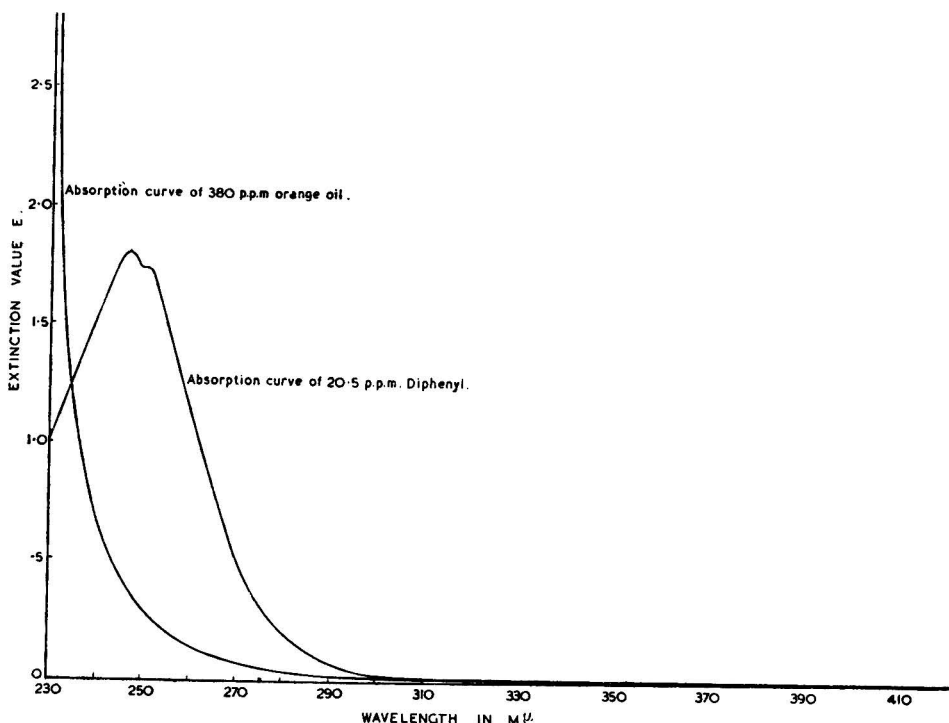


Fig. 1. Absorption curves of 20 p.p.m. diphenyl and 380 p.p.m. orange oil in *cyclohexane*.

EXTRACTION OF DIPHENYL FROM ORANGE PEEL—

The system of extraction used by Tomkins and Isherwood has proved very satisfactory. The peel is minced and steam-distilled and the distillate extracted with *cyclohexane*. Since the solubility of diphenyl in water is very low—less than 1 p.p.m.—three successive extractions of the distillate with *cyclohexane* suffice to remove all but traces of diphenyl. Unfortunately, the orange oil present in the distillate is also extracted by the *cyclohexane*. Orange oil interferes in both the colorimetric method and the absorptiometric method of estimating diphenyl. In the following sections methods of eliminating the interfering effects of orange oil are presented.

THE ELIMINATION OF INTERFERING SUBSTANCES—

When the distillate from 300 g. of minced peel is extracted successively with three 50-ml. portions of *cyclohexane* and the extracts are combined, the solvent normally contains between 3 and 4 per cent. of orange oil, irrespective of the amount of diphenyl present.

Tomkins and Isherwood used successive treatments with concentrated sulphuric acid to destroy the orange oil. Their results were subject to an error of about 20 per cent. It

was found in the course of the present work that not only did the sulphuric acid destroy the orange oil, but it also affected the diphenyl recovery values. This effect is considerable, as indicated in the following tables.

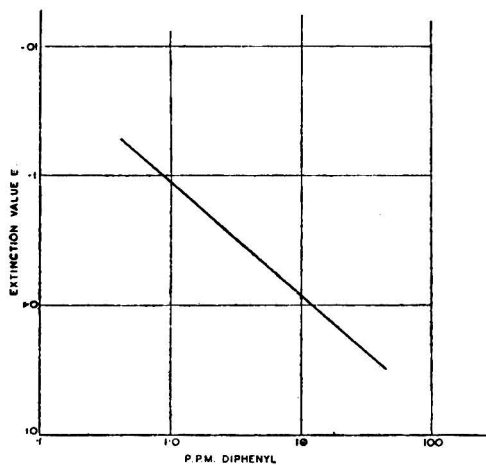


Fig. 2. Working curve for diphenyl in cyclohexane.

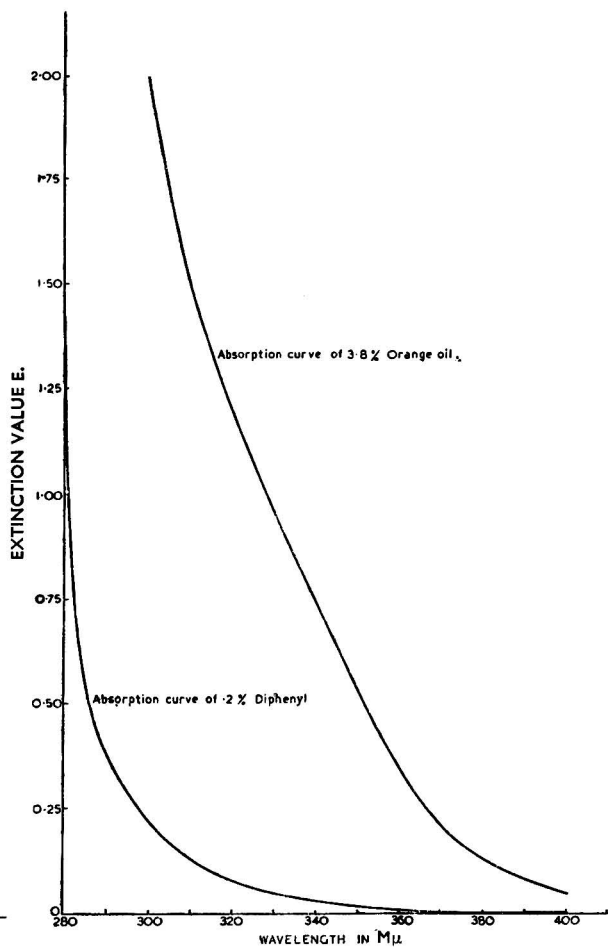


Fig. 3. Absorption curves of 3.8 per cent. orange oil and 0.2 per cent. diphenyl in cyclohexane.

TABLE I

EFFECT OF CONCENTRATED SULPHURIC ACID TREATMENT OF A MIXTURE OF DIPHENYL AND ORANGE OIL IN *cyclohexane* ON DIPHENYL ESTIMATION

Treatment of sample	Mean recovered p.p.m.	Error %
82.2 p.p.m. diphenyl	82.0	-0.24
82.2 p.p.m. diphenyl washed with 2 × 75 ml. of distilled water	82.5	+0.36
82.2 p.p.m. treated with 4 × 20 ml. concentrated sulphuric acid and washed with water	66.6	-19.0
82.2 p.p.m. + 1 ml. of Navel orange oil treated with 4 × 20 ml. sulphuric acid and washed with water	55.3	-32.8
82.2 p.p.m. + 2 ml. of Navel orange oil treated with 4 × 20 ml. sulphuric acid and washed with water	48.3	-41.2

The percentage error increases with every increase in orange oil content.

TABLE II

RECOVERY OF DIPHENYL AFTER CONCENTRATED SULPHURIC ACID TREATMENT OF THE EXTRACT OF THE STEAM-DISTILLATE OF MINCED ORANGE PEEL TO WHICH KNOWN QUANTITIES OF ORANGE OIL AND DIPHENYL HAD BEEN ADDED

No. of oranges	Orange oil added ml.	Diphenyl added to orange oil mg.	Diphenyl in <i>cyclohexane</i> p.p.m.	Recovery value diphenyl p.p.m.	Error %
5	2	16	137.01	93.0	- 32.1
5	1	8	68.5	43.8	- 36.0
5	0.5	4	34.25	27.0	- 21.6

The removal of orange oil from the extract of the steam-distillate by repeated treatments with concentrated sulphuric acid results in considerable losses of diphenyl as well. In view of these results it is probable that the large errors experienced by Tomkins and Isherwood in determining diphenyl by their colorimetric method arose from the successive treatments of the *cyclohexane* extracts with concentrated sulphuric acid.

CORRECTION FOR ABSORPTION BY ORANGE OIL—

In view of the difficulties of removing orange oil from the extracts, the question arises whether the errors introduced in the absorptiometric method by the presence of orange oil can be eliminated by determining the absorption by orange oil at a wavelength where

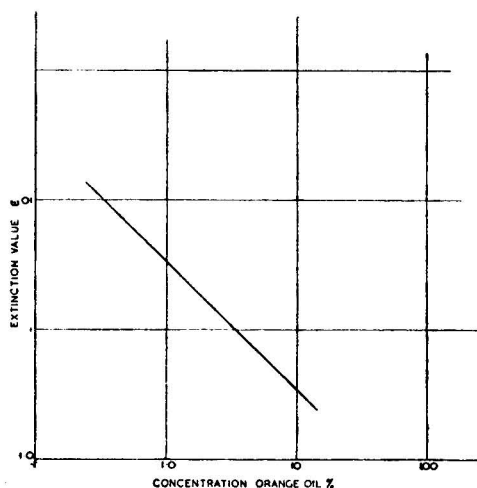
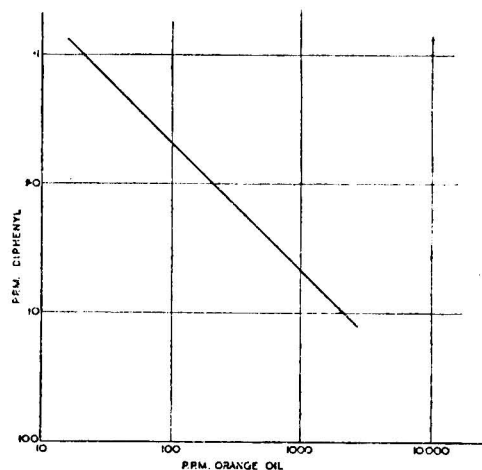


Fig. 4. Working curve for orange oil.

Fig. 5. Curve of relationship between diphenyl and orange oil at 250 $m\mu$.

diphenyl shows little or no absorption, and whether a correction can be applied for the absorption of the orange oil when determining diphenyl at 250 $m\mu$.

In the study of the absorption characteristics of orange oil a sample of oil from Navel oranges was prepared by steam-distillation, and this sample has served as the standard throughout. The absorption characteristics of this oil have not changed during storage for a period of 14 months. All the investigations to date have been confined to Navel oranges, and hence the complicating factor of differences in the oil characteristics due to variety and species is eliminated from the present investigations. Such difficulties will no doubt be found important and necessitate separate calibration curves for different varieties and species of citrus fruits. Experience alone will indicate whether fruit of the same variety grown in different districts will show sufficient differences to call for separate calibration curves.

Fig. 3 indicates the absorption curve between 300 and 400 $m\mu$. of a 3.8 per cent. solution of the "standard" Navel orange oil in *cyclohexane*. On the same graph the absorption curve for a 0.2 per cent. diphenyl solution in *cyclohexane* is also indicated. Since diphenyl shows little or no absorption above 350 $m\mu$., the possibility of using the region above 350 $m\mu$. for assaying orange oil in presence of diphenyl is evident. The wavelength selected for

this purpose is 375 $m\mu$. The E values at 375 $m\mu$. for a range of orange oil concentrations between 0.1 and 10 per cent. are represented by a straight line, see Fig. 4.

Since the extract of the steam-distillate has to be diluted 100-fold for the determination of the absorption of diphenyl at 250 $m\mu$., the absorption curves between 230 to 400 $m\mu$. of a 0.002 per cent. diphenyl solution and of a 0.038 per cent. orange oil solution are presented in Fig. 1. The absorption of diphenyl in the ultra-violet band is clearly defined by the peak at 247 $m\mu$. Orange oil, however, has no peak at or near the diphenyl peak, but the absorption increases rapidly at the shorter wavelengths.

In order to determine the quantities of diphenyl and orange oil giving equal absorption at 250 $m\mu$., the absorption of standard concentrations of orange oil ranging from 0.005 to 0.04 per cent. were determined at 250 $m\mu$.. These values were converted into unit diphenyl values from the calibration curve for diphenyl. The orange oil and diphenyl equivalents thus obtained, when plotted on log-paper, show a linear relationship, Fig. 5.

Provided there is no chemical interaction between the orange oil and diphenyl, the absorption at 250 $m\mu$. will be the same as the constituent absorptions of diphenyl and orange oil at that wavelength, since

$$d = l(\epsilon_1 C_1 + \epsilon_2 C_2 + \dots)$$

where $C_1, C_2 \dots$ are the concentrations of the absorbing substances having molecular extinction coefficients of $\epsilon_1, \epsilon_2, \dots$.⁵

Since the total absorption of mixtures of diphenyl and orange oil in *cyclohexane* agrees very closely with the sum of their separate absorptions, as indicated in Table III, it can be assumed that there is no chemical reaction between the diphenyl and the orange oil, and hence the method is applicable.

TABLE III

Concentra- tions (a) of orange oil %	E value 250 $m\mu$.	Concentra- tions (b) of diphenyl %	E value at 250 $m\mu$.	E value of samples of (a) + (b) at 250 $m\mu$.	Sum of E values of (a) and (b)	Error %
0.03	0.165	0.000257	0.260	0.405	0.425	+ 5.0
0.04	0.215	0.001028	0.900	1.080	1.115	+ 3.1
0.05	0.260	0.000514	0.490	0.740	0.750	+ 1.35
					Mean	3.1%

METHOD ADOPTED

The method adopted for the determination of diphenyl in the presence of orange oil is as follows:—

- Determine the E value of the undiluted *cyclohexane* extract of the steam-distillate of the sample at 375 $m\mu$. and convert into concentration of orange oil from the graph, Fig. 4.
- Convert the value of orange oil obtained in (a) above into the equivalent value of diphenyl by means of the graph, Fig. 6.
- Dilute the *cyclohexane* extract 100-fold. Determine the E value at 250 $m\mu$. and convert into concentration of diphenyl from the graph, Fig. 2.
- Subtract the value obtained in (b) from the value obtained in (c) to obtain the actual amount of diphenyl present.

The accuracy of the method may be gauged from the following data.

Table IV gives the results of an analysis of fifteen mixtures of diphenyl and orange oil analysed by the method adopted, together with the percentage error of each determination.

Known concentrations of diphenyl dissolved in orange oil were made up and added to the minced peel of five test oranges. The distillate, recovered from the steam-distillation, was extracted in *cyclohexane* and the concentration of diphenyl determined. Table V gives the data of this analysis.

Known concentrations of diphenyl dissolved in *cyclohexane* were made up and added to the minced peel of five test oranges, the distillate was extracted, and the concentration of diphenyl determined.

The accuracy of the method depends mainly on the purity of the *cyclohexane*. Benzene present in the sample does not have an appreciable effect on optical density readings taken at 375 $m\mu$., but has a large effect on readings taken at 250 $m\mu$.

TABLE IV
ANALYSIS OF FIFTEEN MIXTURES OF DIPHENYL AND ORANGE OIL WITH
ERRORS OF EACH DETERMINATION

Contents of sample	E value at 375 m μ . (a)	Diphenyl equivalent of orange oil (b)	E value at 250 m μ . (d)	Diphenyl equivalent of (d) in p.p.m. (c)	True diphenyl in p.p.m. (c-b) \times 100	Error %
0.1028% diphenyl						
+5% orange oil	0.182	2.58	1.128	13.0	10.42	+ 1.36
+4% "	0.142	2.00	1.068	12.3	10.30	+ 0.19
+3% "	0.106	1.50	1.041	11.9	10.40	+ 1.17
0.0514% diphenyl						
+5% orange oil	0.178	2.50	0.705	7.72	5.22	+ 1.36
+4% "	0.142	2.00	0.660	7.04	5.05	- 1.95
+3% "	0.105	1.48	0.620	6.60	5.12	- 0.26
0.0257% diphenyl						
+5% orange oil	0.176	2.45	0.480	4.90	2.45	- 2.14
+4% "	0.143	2.05	0.455	4.55	2.50	- 2.70
+3% "	0.104	1.45	0.408	4.02	2.63	+ 2.34
0.0128% diphenyl						
+5% orange oil	0.178	2.50	0.385	3.75	1.25	- 2.34
+4% "	0.142	2.00	0.350	3.38	1.38	+ 7.80
+3% "	0.108	1.58	0.302	2.85	1.27	- 0.78
0.0064% diphenyl						
+5% orange oil	0.176	2.45	0.328	3.05	0.60	- 6.24
+4% "	0.144	2.08	0.293	2.73	0.65	+ 1.56
+3% "	0.107	1.55	0.241	2.17	0.62	- 3.12
				Mean	..	2.3%

TABLE V

RECOVERY VALUES OF DIPHENYL DISSOLVED IN ORANGE OIL ADDED TO MINCED PEEL

Orange oil added ml.	Diphenyl added to peel %	Diphenyl recovered %	Error %
2	0.013701	0.01400	+ 2.2
1	0.006850	0.00690	+ 0.7
0.5	0.003425	0.0035	+ 2.2
		Mean	1.7%

TABLE VI

RECOVERY VALUES OF DIPHENYL DISSOLVED IN *cyclohexane* ADDED TO MINCED PEEL

Diphenyl added to minced peel %	Diphenyl recovered %	Error %
0.01619	0.0160	- 1.2
0.01563	0.0155	- 0.8
0.00757	0.0076	+ 0.4
0.00405	0.00395	- 2.5
	Mean	1.2%

The absorption cells must be rinsed with spectrochemically pure *cyclohexane* after every reading, because a drop containing 0.001 per cent. of diphenyl, left over in the cell, will cause an error of 10 per cent. when a sample of 0.0001 per cent. solution of diphenyl is placed in the cell.

The mean percentage error in adopting this method for the determination of diphenyl in presence of orange oil is 2 per cent.

The method is sensitive enough to determine as little as 0.00002 per cent. (0.2 p.p.m.) of diphenyl in a sample.

SUMMARY

The colorimetric method for the estimation of diphenyl in orange peel as adopted by Tomkins and Isherwood is not sensitive enough to correlate diphenyl content with its preserving action, since the percentage error is of the order of 20 per cent. A more accurate method is desired. The procedure for the extraction of diphenyl from the orange peel is based on their work, but for the actual determination of diphenyl another method had to be evolved.

A spectrophotometric method was suggested by Cox, using *cyclohexane* as a solvent for the determination of diphenyl at 251 $m\mu$. The present work shows that when diphenyl is dissolved in *cyclohexane* and the absorption curve is determined between 230 and 400 $m\mu$., the maximum absorption lies at 247 $m\mu$. with an $E_{1\%}^{1\text{cm}}$ value of 1100. Since the absorption of diphenyl is constant between 249 and 251 $m\mu$., working curve values are taken at 250 $m\mu$.. The maximum concentration of diphenyl that can be determined is 20 p.p.m. For higher concentrations suitable dilutions can be made.

To eliminate the interfering effect of orange oil in the absorption of diphenyl at 250 $m\mu$., sulphuric acid was used to destroy it. The use of sulphuric acid, however, results in too low diphenyl values.

The following method was evolved for the determination of diphenyl in presence of orange oil.

Since orange oil shows absorption between 280 and 400 $m\mu$. and diphenyl no absorption above 350 $m\mu$., the concentration of orange oil can be determined by its absorption at 375 $m\mu$. in the undiluted *cyclohexane* extract. The absorption at 250 $m\mu$. after diluting 100-fold indicates the concentration of diphenyl plus orange oil; the concentration of the latter being obtained from the linear relationship between diphenyl and orange oil from the extraction of the latter at 375 $m\mu$.

Recovery tests as carried out show a mean percentage error of 2 per cent.

We wish to thank the Director of the Low Temperature Research Laboratory, Cape Town, Mr. Rees Davies, for valuable criticism and guidance; Mr. A. G. Visser for the drawing and Mr. D. J. de Villiers for the photographing and printing of the figures, and Dr. H. M. Schwartz of the C.S.I.R., Chemistry Department, University of Cape Town, for the use of their Beckman photometer.

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Analysis of Rare Earth Oxides by means of Emission Spectra

Part I. Persistent Lines in Arc Spectra of Rare Earth Elements

BY D. M. SMITH AND G. M. WIGGINS

(Paper presented at the Joint Meeting of the North of England Section and the Physical Methods Group at Liverpool, on October 2nd, 1948)

THE analysis of rare earth oxides by means of their arc emission spectra presents a number of difficulties on account of the great complexity of these spectra. This is particularly evident when an examination is made for other rare earth elements occurring as impurities. This paper and the one following record the results of investigations, carried out over a period of some two years, on the following problems—

1. The empirical determination of the most persistent lines of rare earth elements, for a given type of arc excitation. A preliminary note on this subject was published in this journal in 1946.¹

2. The identification of faint lines coinciding with impurity lines.
3. Methods for avoiding the masking effects due to the presence of cyanogen bands in graphite and carbon arc spectra. (A method, using a carbon arc in steam, giving practically complete elimination of these bands is described in Part II.)

ARC EXCITATION SOURCES—

At the time these investigations were started the only satisfactory arc source available in the Company's laboratory was an intermittent A.C. arc, a low-voltage A.C. arc triggered by means of a superimposed high-frequency low-energy spark occurring at the voltage peak of the A.C. wave (modified from B.S. 1225 : 1945). Since this type of arc had proved suitable in other cases of trace analysis, an arc between pure graphite electrodes, taking 7 amp., was first used for the analysis of rare earth oxides.

Subsequently two D.C. arc sources became available, and these were tested in comparison with the intermittent A.C. arc. One was a simple D.C. arc circuit, 100-volt open circuit voltage, obtained by half-wave rectification of A.C., smoothed with a suitable choke. The other was the Hilger constant-current D.C. arc source, the current strength being 5.6 amp.

The arc gap in each case was 3 mm.

EMPIRICAL DETERMINATION OF THE MOST PERSISTENT LINES OF THE RARE EARTH ELEMENTS

It was concluded from a study of the available data on persistent lines of the rare earth elements^{2,3,4,5} that the empirical determination of the most persistent lines, under the conditions of arc excitation used for the analysis of rare earth oxides, was a necessary preliminary investigation.¹

This was done by photographing successive exposures of a continuously burning arc until the whole of the material had been volatilised, using as electrode materials both pure graphite and pure silver rods. This investigation was mainly carried out with the intermittent A.C. arc. Also, drops of dilute chloride solutions evaporated on the electrodes have been used to give faint spectra of the rare earth elements, showing only the principal sensitive lines. The latter method was also used to provide superposed (overlapping) comparison spectra to assist in the recognition of impurity lines (and coincidences) in the spectra of the rare earth oxides (see Fig. 3*b*).

A Hilger Fully Automatic Littrow spectrograph was used to record the spectra, and was set for the region 2960 to 6000 Å., since according to Meggers⁶ the most persistent lines were expected to be found in this wavelength region. Ilford Special Rapid Panchromatic plates were used, these being sensitive over the whole range studied and also suitable in other respects. In subsequent tests a wider range of spectrum was examined, using photographic plates with appropriate emulsions.

The results obtained are given below in Table I and, for comparison, hitherto unpublished results by Meggers and Scribner, of the National Bureau of Standards, Washington,* are also included. The latter results were derived from similar observations to determine the strongest lines of 70 elements, including rare earths, excited in a 220-v., 10-amp. D.C. arc between copper electrodes, containing one or more of the elements in atomic ratios of 1000 to 1. The authors are indebted to Dr. Meggers for kindly making these results available, thus providing an authoritative check on their own observations.

Whilst there is a considerable measure of agreement between the two sets of data, occasionally there are marked discrepancies, *e.g.*, in the assignment of the most persistent line of neodymium. As suggested by Meggers,* this may be due to differences in excitation sources. According to Gerlach and Reidl² the relative intensities of lines are strongly influenced by the nature of the discharge for dysprosium, erbium, terbium and thulium. Variation in the sensitivities of different plates to light of different wavelengths may also have been a contributory cause.

Some difficulties were experienced in deciding, by visual estimations of intensity, on the relative sensitivities of the lines. For example, in many instances the intensities were nearly equal at the threshold value of the plate, particularly for the less persistent lines. Moreover, some lines may have been slightly enhanced in intensity by being superimposed on the spectrum background associated with strong silver and copper lines.

* Private communication.

Only three lines are quoted for ytterbium, as these are much stronger than the other two quoted by Meggers and Scribner.

TABLE I
THE MOST PERSISTENT LINES OF RARE EARTH ELEMENTS*

Wavelength	Intensities		Sensitivity		
	Arc	Spark	M. and S. (D.C.)	Authors (A.C.) (D.C.)	
1. CERIUM					
4186-599 II	80	25	U1	U1	U1
4137-646 II	25	12	U3	U3	U3
4133-800 II	35	8	U2	U2	U2
4040-762 II	70	5	U5	U5	U4
4012-388 I, II	60	20	U4	U4	U4
3942-151 II	35	8	—	—	U4
3801-529 II	25	3	—	—	U5
The intensities of the lines 4012-388 and 4040-762 A. are almost equal in the A.C. arc; the intensities of the last four lines are almost equal in the D.C. arc.					
2. DYSPROSIUM					
4211-719 I	200	15	U2	—	U5
4186-810 I	100 w	12	U3	—	—
4045-983 I	150	12	U4	U3	—
4000-454 II	400	300	—	—	U5
3968-395 II	300	—	U5	—	—
3944-692 II	300	150	—	U5	U4
3645-416	300	100	—	U2	U2
3531-712	100	100	U1	U1	U1
3407-80	150	9	—	U4	U3
Dy 3968-395 is masked by Ca 3968-468 in all spectra photographed in the authors' laboratory.					
Dy 4211-719 is masked by Ag 4210-936 in A.C. silver arc spectra.					
Dy 3531-712 is much enhanced in A.C. arc spectra as compared with D.C. arc spectra.					
3. ERBIUM					
4007-967 I	35	7	U4	U4	U3
3906-316 II	25	12	U5	U3	U3
3692-652	20	12	U2	U2	U2
3499-104	18	15	U3	U4	U3
3372-750	35	20	U1	U1	U1
4. EUROPIUM					
4205-046 II	200 R	50	U2	U2	U2
4129-737 II	150 R	50 R	U3	U3	U3
3971-99 I	1000 Rwh	—	U5	U5	U5
3930-503 II	1000 R	400 R	U4	U4	U4
3819-66 II	500 wd	500 wd	U1	U1	U1
5. GADOLINIUM					
3768-405	20	20	U4	U4	U4
3646-196	200 w	150	U5	U4	U5
3422-466	80	100	U1	U1	U1
3362-244	150	180	U2	U2	U2
3350-482	150	180	U3	U3	U3
6. HOLMIUM					
4103-84 I	400	400	U4	U4	U3
4053-92 I	400	200	U5	—*	U5
3891-02 II	200	40	U2	U2	U2
3796-73	20	40	U3	U5	U4
3456-00	60	60	U1	U1	U1
3398-98	40	60	—	U3	U5

* Ho 4053-92 is masked by Ag 4055-624 in A.C. arc spectra.

* Wavelengths and intensities are taken from the *M.I.T. Wavelength Tables*. The notation for the sensitivity of the lines follows the same convention as in these tables, U1 denoting the most persistent line.

Wavelength	Intensities		Sensitivity		
	Arc	Spark	M. and S. (D.C.)	Authors	
				(A.C.)	(D.C.)
7. LANTHANUM					
4086-714 II	500	500	U3	U3	U5
3988-518 II	1000	800	U2	U2	U2
3949-106 II	1000	800	U1	U1	U1
3794-773 II	400	200	U5	U5	U4
3790-822 II	400	300	U4	U4	U3

Except for La 3949-106 (U1) the above lines are of nearly the same intensity.

8. LUTECIUM					
3507-39 II	100	150	U4	U3	U3
3397-07 II	50	20 r	—	U4	—
3359-56 I	150	15	U5	U4	U4
3077-60 II	100	200	U3	U5	U5
2911-39 II	100	300	U2	U2	U2
2615-42 II	100	250	U1	U1	U1

Sensitive lines of wavelength shorter than 2960 Å. were determined from spectra photographed with a medium size spectrograph (Hilger flat-field).

9. NEODYMIUM					
4303-573 II	100	40	U1	U4	U5
4156-083 II	10	20	U4	U5	U4
4109-455 II	30	30	U5	U3	U3
4061-085 II	40	30	U3	U2	U2
4012-250 II	80	40	U2	U1	U1

The first three lines (4303 to 4109) appear of almost equal intensity.

10. PRASEODYMIUM					
4225-327 II	50	40	U4	U4	U3
4222-98 II	125	40	U5	U3	U5
4179-422 II	200	40	U2	U5	U4
4100-746 II	200	50	U3	U2	U2
3908-431 II	100	60	U1	U1	U1

Except for Pr 3908-431 (U1) the above lines are of nearly the same intensity.

11. SAMARIUM					
3885-284 II	50	50	U5	U5	U5
3634-271 II	100	25	U4	U3	U3
3609-484 II	60	100	U3	U1	U2
3592-595 II	40	50	U2	U2	U1
3568-258 II	40	50	U1	U4	U4

The most sensitive lines, U1 to U4, appear with almost equal intensity.

12. TERBIUM					
3874-18 II	200	200	—	U5	*
3676-35	100	200	U3	U3	
3585-03	15	50	U2	—†	
3561-74	200	200	U4	U2	
3509-17	200	200	U1	U1	
3324-40	70	50	U5	U4	

* No sample available for test with the D.C. arc.

† No sensitive line at wavelength 3585-03 Å. was detected in intermittent A.C. arc spectra.

13. THULIUM					
3848-018	400	250	U2	U1	*
3795-765	250	150	U5	—	
3717-92	100	10	U1	U3	
3462-20	250	200	U3	U2	
3425-08	200	300	U4	U4	
3362-61	250	200	—	U5	

* No sample available for test with the D.C. arc.

Note—The order of sensitivity has not been established with certainty for the thulium lines as the only samples available were very impure. Tm 3425-08 and 3362-61 Å. are of almost equal intensity.

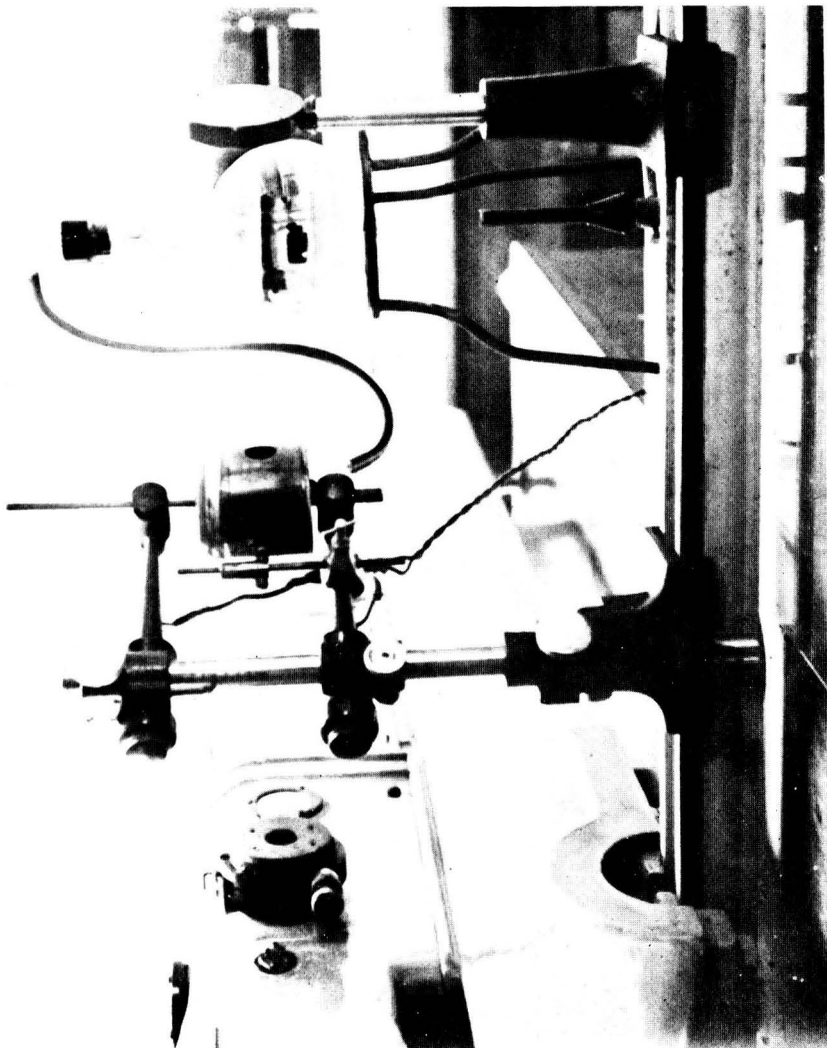
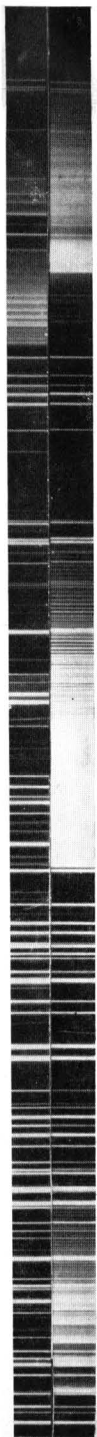
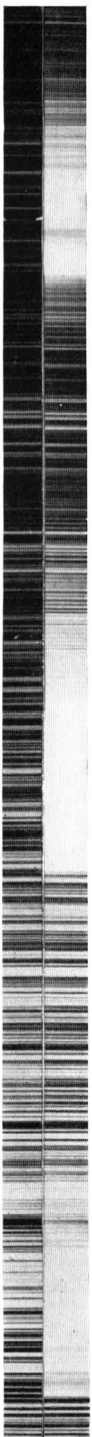


Fig. 1. Apparatus for the Carbon Arc in Steam.

LANTHANUM OXIDE



CERIUM OXIDE



NEODYMIUM OXIDE

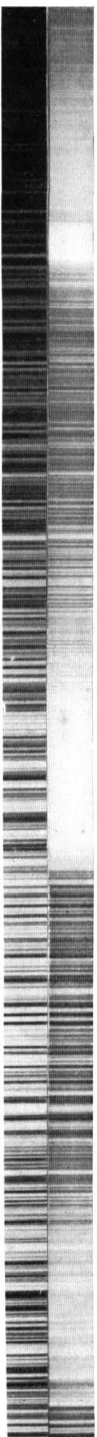


Fig. 2. Arc spectra of rare earth oxides. The upper spectrum, in each case, is of the arc in air and the lower spectrum of the arc in steam, showing the suppression of the cyanogen bands by the latter method of excitation. (Region of spectrum: 3500 to 4230 \AA .)

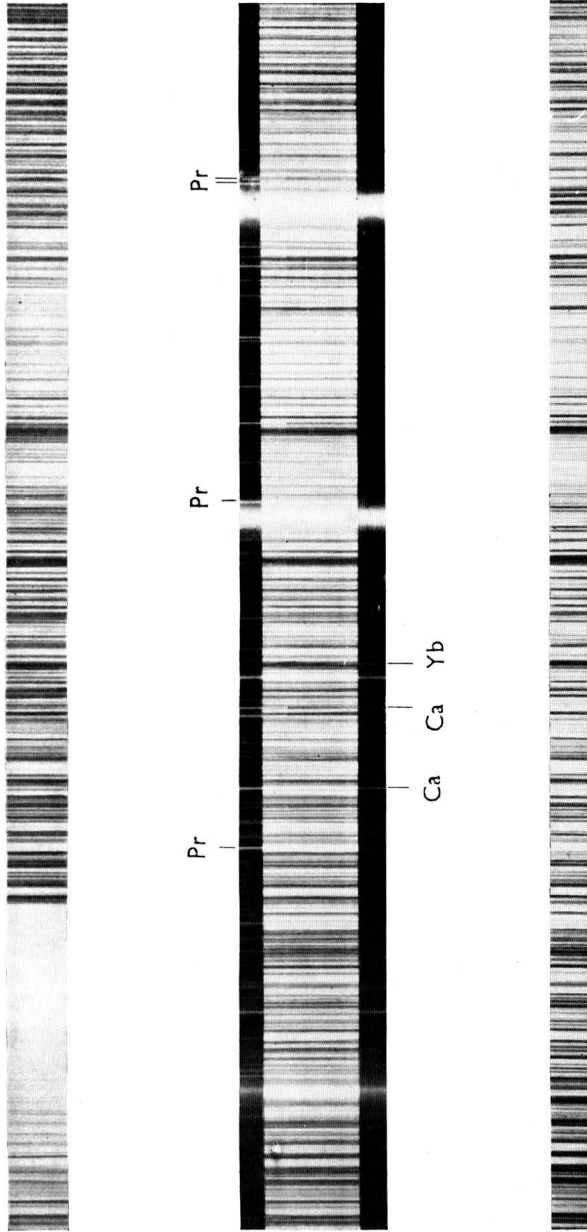
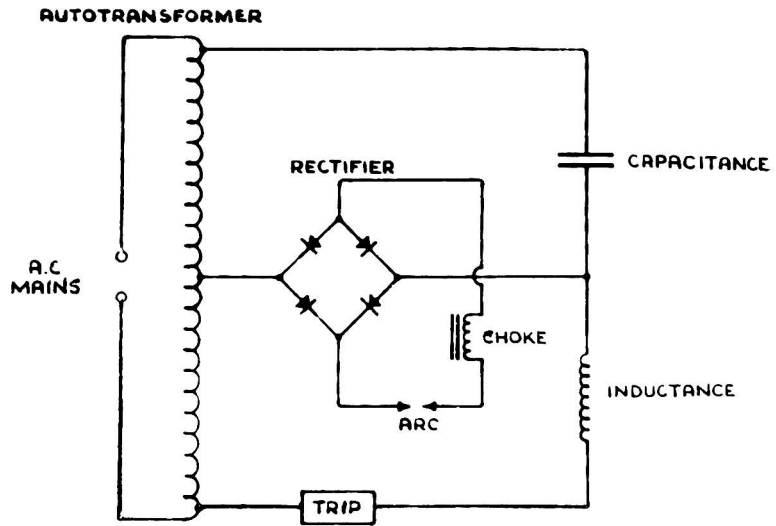


Fig. 3. Arc spectra of cerium oxide (3800-4300 Å.) obtained with different electrode materials.
 (a) Graphite arc in air.
 (b) Silver arc in air (illustrating the use of overlapping comparison spectra).
 (c) Carbon arc in steam.



CIRCUIT DIAGRAM OF CONSTANT
CURRENT D.C. ARC

Fig. 4

TABLE I—*continued*

Wavelength	Intensities		Sensitivity		
	Arc	Spark	M. and S. (D.C.)	Authors	
				(A.C.)	(D.C.)
14. YTTERBIUM					
7699.49	2000	—	U5	—	—
5556.476 I	1500	50	U4	—	—
3987.994 I	1000 R	500 R	U3	U3	U3
3694.203 II	500 R	1000 R	U1	U2	U2
3289.37 II	500 R	1000 R	U2	U1	U1
Yb 3289.37 may be slightly enhanced by the background due to Ag 3280.683.					
15. YTTRIUM					
4374.935 II	150	150	U2	U3	U5
4102.376 I	150	30	U5	U5	—
3774.332 II	12	100	U3	U2	U2
3710.290 II	80	150	U1	U1	U1
3600.734 II	100	300	U4	U4	U3
3242.280 II	60	100	—	U5	U4

Y 4374.935 appears as a broad diffuse line at low intensities.

IDENTIFICATION OF CERTAIN FAINT LINES IN THE SPECTRA OF RARE EARTH ELEMENTS AS BEING DUE TO OTHER RARE EARTH ELEMENTS PRESENT AS IMPURITIES

For the identification of impurity lines in rare earth spectra the standard reference book used has been the *M.I.T. Wavelength Tables*. Certain faint lines, attributed in these tables to the rare earth element under test, coincide in position with those of strong lines in the superposed comparison spectra of the impurity rare earth elements sought. Such coincidences, briefly referred to as "Significant Coincidences," are listed in Table II. The close agreement between these wavelengths and those of the strongest lines of other elements supports the conclusion that the lines in question are in fact sensitive rare earth impurity lines. In justification of this view it may be noted that in the *M.I.T. Wavelength Tables* (p. xi, "Precision of Wavelengths") it is suggested that the wavelengths of lines due to rare earths of especial rarity may not be entirely above suspicion. Moreover, the faint lines given in Table II are not recorded in the wavelength tables published by Gatterer and Junkes⁵ (which were not available to the authors until the completion of the present work).

In the case of erbium, for example, the holmium line 3456.00 A. and the ytterbium line 3289.37 A. are the only lines coinciding with faint erbium lines, and these lines are shown in Table I (6, 15) as the most persistent lines of these impurity elements. The same applies to europium containing ytterbium as an impurity.

It may be noted that no impurity coincidences are listed in Table II, *infra*, for La, Lu, Tm and Yb. The data for these elements have been censored by Dr. W. F. Meggers for the *M.I.T. Wavelength Tables*.

FORTUITOUS COINCIDENCES

Further coincidences are recorded in Table III, but as the lines in the first column are assigned to the corresponding elements in the tables published by Gatterer and Junkes, these coincidences are to be regarded as fortuitous.

The data in Tables II and III are not claimed to be exhaustive lists; they record those coincident lines that will most commonly occur when the M.I.T. Tables are used for the analysis of rare earth oxides and that have been studied in connection with the present work. They are given here with the object of assisting others engaged on similar work.

METHODS FOR INCREASING THE SENSITIVITY OF DETECTION OF ONE RARE EARTH IN ANOTHER

Because the cyanogen bands in the carbon or graphite arc spectra masked a number of the persistent lines of the rare earth elements, an intermittent A.C. arc taking from 8 to 10 amp. between pure silver electrodes has been used as a routine method of analysis. The graphite arc method, however, was satisfactory for the detection of common impurities in rare earth oxides.

TABLE II

(Tentative identification of certain recorded faint lines as sensitive impurity lines)

Recorded faint lines			Coincident sensitive lines			
Element and wavelength	Intensity		Element and wavelength	Intensity		Sensitivity
	Arc	Spark		Arc	Spark	
CERIUM						
3995-752	6	—	La II 3995-750	600	300	—
3988-518	8 h	—	La II 3988-518	1000	800	U2
3987-990	5	—	Yb I 3987-994	1000 R	500 R	U3
3219-948	2	—	Tb 3219-95	50	50	—
DYSPROSIUM						
4040-76	6	—	Ce II 4040-762	70	5	U5
3634-27	3	3 h	Sm II 3634-271	100	25	U3, 4
3494-78	2	—	Ho 3494-77	30	40	—
ERBIUM						
4086-713	8 s	—	La II 4086-714	500	500	U3
4077-970	20 s	18 s	Dy 4077-974	150 r	100	—
4061-082	5	—	Nd II 4061-085	40	30	U2, 3
4031-690	6 w	—	La II 4031-692	400	300	—
4012-253	12	—	Nd II 4012-250	80	40	U1, 2
4000-452	35	6	Dy II 4000-454	400	300	U5
3941-515	5	—	Nd 3941-512	60	30	—
3710-290	15 wh	8 wh	Y II 3710-290	80	150	U1
3531-714	40	25	Dy 3531-712	100	100	U1
3494-494	15	9	Dy 3494-496	100	5	—
3456-003*	25 d	10 d	Ho 3456-00	60	60	U1
3289-36	25	8	Yb II 3289-37	500 R	1000 R	U1, 2
EUROPIUM						
3462-21	5	1 h	Tm 3462-20	250	200	U2, 3
3289-38	2	—	Yb II 3289-37	500 R	1000 R	U1, 2
HOLMIUM						
4007-96	4	3	Er I 4007-967	35	7	U4
4000-45	5	5	Dy II 4000-454	400	300	? U5
3988-00	—	6	Yb I 3987-994	1000 R	500 R	U3
3898-55	6	8	Dy 3898-544	100	—	—
3692-65	10	15	Er 3692-652	20	12	U2
3645-41	8	8	La II 3645-414	100	60	—
3600-73	6	—	Dy 3645-416	300	100	? U2
3289-38	10	20	Y II 3600-734	100	300	U4
			Yb II 3289-37	500 R	1000 R	U1, 2
NEODYMIUM						
3306-375	12	12	Sm II 3306-372	100	40	—
SAMARIUM						
4133-797	2	—	Ce II 4133-800	35	8	U2
3819-678	10	20	Eu II 3819-66	500 wd	500 wd†	U1
TERBIUM						
4186-60	2	—	Ce II 4186-599	80	25	U1
4077-97	25	2	Dy 4077-974	150 r	100	—
YTRIUM						
3694-20	4	—	Yb II 3694-203	500 R	1000 R	U1, 2
3372-77	15	3	Er 3372-750	35	20	U1

* Double line; one probably a faint erbium line, although no erbium line of this wavelength is recorded by Gatterer and Junkes.

† Double line.

The silver arc gave weaker spectra than either the carbon or graphite arcs. Tests were also made with pure copper electrodes, but these proved no better in this respect. It was found that moistening the oxide with a drop of nitric acid just before making the exposure resulted in stronger spectra. Even so, the method was not sufficiently sensitive for the

TABLE III
FORTUITOUS COINCIDENCES (M.I.T. WAVELENGTH TABLES)

Faint lines			Coincident sensitive lines		
Element and wavelength	Intensity		Element and wavelength	Intensity	
	Arc	Spark		Arc	Spark
DYSPROSIUM					
3456.01	40	—	Ho 3456.00	60	60
3327.88	2	—	Y II 3327.875	60	60
3242.285	4	—	Y II 3242.280	60	100
GADOLINIUM					
4222.98 II	10	—	Pr II 4222.98	125	40
EUROPIUM					
3710.29 II	20 w	1 wh	Y II 3710.290	80	150
3319.887 II	20	5	Dy 3319.887	150	9
HOLMIUM					
3319.87	6	6	Dy 3319.887	150	9
3216.67	—	8	Y II 3216.682	40	70
NEODYMIUM					
4424.343	50	50	Sm II 4424.342	300	300
3930.506	20	30	Eu II 3930.503	1000 R	400 R
3592.595 II	20	30	Sm II 3792.595	40	50
3531.712 II	6	4	Dy 3531.712	100	100
3456.004 II	4	—	Ho 3456.00	60	60
PRASEODYMIUM					
3795.765	30 d	20 d	Tm 3795.765	250	150
TERBIUM					
3455.99	8	—	Ho 3456.00	60	60
3100.51	15	8	Gd 3100.508	100	80
YTTERBIUM					
4409.34 II	6	10	Sm II 4409.337	100	100

detection of some rare earths when present as impurities. The lack of sensitivity was confirmed by failure to detect such elements in samples known to contain rare earth impurities by the variations in colour, a sensitive test in certain cases.

It was therefore concluded that the carbon arc would provide the highest sensitivity of detection if the cyanogen bands could be suppressed. The successful solution of this problem is described in Part II.

Part II. A Technique for the Suppression of Cyanogen Bands in Carbon Arc Spectra of Rare Earth Oxides

By G. M. WIGGINS

IN the course of the work on empirical determination of the most persistent lines of the rare earth elements, reported in Part I of this paper, it was concluded that the arc (either A.C. or D.C.) between pure silver electrodes was less sensitive in detecting impurities than that between pure carbon or graphite electrodes. Since the "cyanogen" bands (the violet system due to the diatomic molecule CN) appear strongly in the region 2960 to 6000 Å., where most of the sensitive lines of the rare earth elements occur, various attempts were made to suppress the emission of these bands by running the arc in a nitrogen-free atmosphere.

CARBON ARC IN STEAM

The simplest atmosphere to produce was water vapour and a simple steam chamber to surround the electrodes was constructed (see Fig. 1). A small aluminium can with a removable lid was used, with holes to admit the electrodes and to provide a steam inlet. An asbestos sheet was fitted on the lid to provide heat insulation. The steam was produced

from a flask of boiling water, about 1 litre in capacity. At first the can was fitted with a quartz window, the steam escaping through the crevices in the holes admitting the electrodes. This window was later found to be superfluous, however, as the quantity of steam produced was sufficient to expel the air from the chamber completely.

A D.C. arc, giving 8 amp. at approximately 100 volts, was obtained between carbon electrodes. The rare earth sample was tamped into a cavity, 1 mm. in diameter and 5 mm. deep, drilled in the lower, negative electrode. The discharge was focused on the slit of a Littrow spectrograph by means of a concave mirror, the arc being offset 8 cm. from the optical axis at a distance of 25 cm. from the slit and the mirror 45 cm. from the slit.

Since the discharge was remarkably brilliant, Ilford Thin Film Half-tone plates were used in place of the Special Rapid Panchromatic plates previously used. The spectrograph slit width was 0.005 mm. These conditions gave maximum resolution of the spectrum lines, the relatively slow speed of the photographic emulsion being more than compensated for by the greatly increased luminosity of the arc discharge in steam as compared with the arc in air.

Three exposures were made, of 10, 20 and 30 seconds respectively, in order to detect faint impurity lines over the whole range of spectrum photographed, the shortest exposure facilitating the detection of such lines in the crowded part of the spectrum.

Fig. 2 illustrates the effective suppression of the cyanogen bands in the spectra of the oxides of lanthanum, cerium and neodymium. A comparison of spectra obtained with the use of graphite and silver electrodes (arc in air) and the carbon arc in steam is shown in Fig. 3.

MECHANISM OF THE ARC

Carbon rods of commercial purity were used for the preliminary tests. On first striking the arc an intense blue discharge is obtained, characteristic of the carbon arc, and the electrodes cannot be opened to more than a millimetre or so without breaking the arc. It was observed that the rare earth sample rapidly fuses into a small globule which remains at the bottom of the deep hole. Both carbon rods burn rapidly until the cathode spot reaches the molten globule. Then the globule appears to flow over the surface of the electrode and volatilisation proceeds steadily. At this stage the arc length can be greatly increased and the arc colour changes to that characteristic of the particular oxide. The exposure is timed from the appearance of this colour.

However, subsequent tests made with high-purity carbon or graphite were unsuccessful; the globule did not flow over the electrode surface and was ejected as soon as it was touched by the cathode spot.

It was at first thought that the type of carbon was a critical factor in the successful operation of the method, particularly as the rod of commercial purity had a fine-grain, almost vitreous, structure of the fractured surface. Attempts were made to match the carbons originally used, the supply of which had become practically exhausted, and some similar material was obtained through the co-operation of Mr. B. S. Cooper, of the Research Laboratories of the General Electric Company Ltd., Wembley. This material also proved unsatisfactory.

The arc spectrum of the original carbon showed strong lines due to sodium, silicon, aluminium and iron. Tests were accordingly made on an intimate mixture of the rare earth oxide with finely divided pure silica. Admixture with pure alumina was also tried, but in both cases only intermittent volatilisation was produced. Finally, trials with addition of sodium silicate proved successful in producing the original type of globule which flowed over the electrode surface.

The method finally adopted is as follows. A small quantity of sodium silicate solution (about 2 drops of a concentrated solution, sufficient to wet the sample) is added to the rare earth oxide and evaporated to dryness, and the resulting powder carefully ground to give a homogeneous mixture. The ratio of sodium silicate to rare earth does not appear to be critical, providing that the proportion of sodium silicate is not excessive.

The prepared sample is then pressed into a cavity $\frac{1}{4}$ -inch deep and of $\frac{1}{8}$ -inch diameter drilled in a $\frac{1}{4}$ -inch diameter carbon rod and this is made the anode. The Hilger constant-current D.C. arc source,* taking 5.6 amp., was used for the excitation of the spectra (see Fig. 4), as this type of arc automatically compensates for sudden changes in arc resistance which take place during the running of the arc, thereby maintaining a steady discharge.

* A tuned circuit containing capacity and self-inductance developed in 1946 (see ref. 1).

On striking the arc in the atmosphere of steam the characteristic yellow sodium flame is observed and this persists for a minute or so. During this period the arc is focused on the slit (with the shutter closed). When the sodium has been completely volatilised the arc colour changes to the intense colour characteristic of the rare earth oxide under test. This rapidly becomes stable and the shutter is opened and the exposure made. For the first tests made with the original carbon rods, using the simple D.C. arc, the oxide sample was placed in a cavity in the cathode. In the final method adopted (constant-current D.C. arc) the sample was made the anode, as this gave more rapid volatilisation of the sodium, resulting in quicker stabilisation of the discharge.

The method of mixing the sample with sodium silicate bears some resemblance to that used by Foster⁷ in an attempt to devise a satisfactory general system of spectrographic micro-analysis. Foster used powdered graphite impregnated with 0.2 ml. of a standard sodium silicate solution and tests with known small additions of silver, nickel and bismuth showed a high sensitivity of detection. He concluded that this sensitivity was due to the formation of a large-area anode spot, so that the whole of the sample took part in the discharge, the rate of distillation being relatively slow, thereby increasing the emission from each atom.

The mechanism of the arc used for the analysis of rare earth oxides, however, appears to be somewhat different, as an extended anode spot is not formed. (Moreover, no powdered graphite is added to the sample.) It is possible that the function of the sodium silicate is that of a flux combining with the oxide in some way to give a substance that volatilises more uniformly in the arc.

STANDARDISED TECHNIQUE

Preparation of sample—A drop of pure sodium silicate solution is added to about 10 to 20 mg. of the sample of rare earth compound (in general, the oxide); the mixture is evaporated to dryness and thoroughly mixed by grinding with an agate pestle and mortar.

Arc electrodes—Pure carbon rods $\frac{1}{4}$ inch in diameter. The powder is tamped into a cavity, $\frac{1}{4}$ -inch deep and of $\frac{1}{8}$ -inch diameter, drilled in the lower, positive electrode.

Arc excitation—Constant-current D.C. arc (Hilger), taking 5.6 amp., the discharge taking place in an atmosphere of steam. (A simple D.C. arc, taking 8 amp., may be used as an alternative, but it is less convenient in operation.)

Arc gap—3 mm.

Spectrograph—Fully automatic Littrow spectrograph, set for the wavelength range 2960 to 6000 Å.

Slit irradiation—The central portion of the arc discharge is focused on the slit by means of a surface-aluminised concave mirror.

Slit width—0.005 mm.

Photographic plate—Ilford Thin Film Half-tone.

Exposure times—Three exposures of 10, 20 and 30 seconds respectively, when the arc has become stabilised.

Plate development—3 minutes in I.D.2 developer, with simple dish-rocking.

SENSITIVITY OF THE METHOD

Owing to the rarity and high cost of materials it has not been possible to carry out extended systematic tests to determine the limits of spectrographic detection of one rare earth as an impurity in another. Some samples with known additions were available, however, and these in conjunction with information supplied by those skilled in the refining of rare earth compounds have given the following indications. Dysprosium, gadolinium, lanthanum, lutecium, yttrium and ytterbium may be detected at concentrations of less than 0.1 per cent., and with these elements erbium, europium and holmium may probably be placed. According to Gatterer and Junkes⁸ as little as 0.0005 per cent. of europium can be detected in solutions of samarium chloride, and from 0.01 to 7 per cent. accurately determined by means of a D.C. arc, taking 3.75 amp., between pure carbon electrodes.

Cerium, neodymium, praseodymium and samarium appear to be much less sensitive and thulium has not yet been studied.

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DISCUSSION

Dr. W. F. ELVIDGE, with reference to the authors' method of eliminating cyanogen bands, which are always a nuisance in spectroscopy, asked if the authors had any experience as to whether their method using sodium silicate could be used in ordinary search for trace elements, particularly in those cases where the lines sought occur among the cyanogen bands.

Mr. D. M. SMITH, in reply, said they had only tried the mixture with sodium silicate in the detection of traces of rare earth element impurities in rare earth oxides. Specially prepared pure sodium silicate was used, but for this purpose the ordinary impurities, traces of which were no doubt present, were of no consequence. In the testing of other materials, however, such traces might vitiate the results, as it appeared to be extremely difficult to prepare spectrographically pure sodium silicate. On the other hand, there seemed to be no reason why the method should not be of fairly general application (with the customary blanks for comparison). He would suggest that it might be applied to the analysis of refractory oxides, such as those of titanium and zirconium.

Mr. J. HASLAM asked if the method for the exclusion of cyanogen bands could be applied to the direct determination of small amounts of impurities in plastic materials.

Mr. B. S. COOPER said that he had been using a method of running an arc in a special atmosphere which had some similarities with that described by Mr. Smith. In his experiments, however, they were using samples rich in silicon and the serious masking of faint lines was caused by the presence of SiO bands. Fortunately their interest was in a region of the spectrum remote from the CN bands, so they went to the other extreme, and instead of eliminating nitrogen, eliminated oxygen by using an atmosphere of nitrogen obtained from a cylinder. The enclosure round the arc was very similar to the authors'. This method proved most effective in eliminating the SiO bands and enabled microphotometer measurements to be made on faint impurity lines in the 2800 to 2400 Å region. A similar method had proved useful in dealing with samples rich in germanium.

With regard to Mr. Haslam's question as to whether the authors' method could be extended to deal with impurities in plastics, Mr. Cooper said that the silicon samples to which he had just referred were arced in the form of pellets. These were made in a hot mould from a mixture of the sample with an excess of pure graphite powder and a plastic binder. They arced quite satisfactorily, so there appeared to be no reason why the same method should not be used to determine impurities in plastics themselves.

Mr. E. VAN SOMEREN asked whether, in view of the greater dispersion available, it would be advisable or preferable to use a glass spectrograph or spectrometer with camera attachment for the analysis of rare earth compounds.

Dr. J. A. C. McCLELLAND observed that as a large proportion of the lines used by the authors, and those used in his own work, did not occur in the visible part of the spectrum, a glass prism instrument would be quite unsuitable. The best instrument to use would be a grating spectrograph. Mr. D. M. SMITH confirmed these statements and added that the most persistent lines of some rare earth elements appeared in the ultra-violet part of the spectrum; in the case of lutecium (Lu II 2615.42 and 2911.39) the lines are far removed from the violet end of the visible spectrum.

The Determination of Copper in Nickel-bearing Steels and Cast Irons: a Photometric Method

By S. D. STEELE AND L. RUSSELL

VARIOUS reagents capable of producing coloured compounds on reaction with copper in solution^{1,2} have been applied to the determination of copper by photometric methods. Of these, sodium diethyldithiocarbamate has been found the most suitable for the determination of copper in ferrous alloys and is probably the one most widely used at the present time for this purpose. It is generally recognised, however, that when it is applied to the determination of copper in ferrous materials, precautions must be taken to prevent interference from iron, either by removal of that element from solution with ammonium hydroxide, or by the production and measurement of the copper diethyldithiocarbamate colour solution at a *pH* greater than 9.0.³ Similar difficulties are associated with the presence of nickel in solution, and various suggestions for the removal of nickel interference have appeared in published reports, as for example, the preliminary separation of nickel by dimethylglyoxime,^{4,5} the separation of copper by means of sodium thiosulphate or hydrogen sulphide, and the extraction of copper by dithizone and carbon tetrachloride.²

In the authors' laboratories, prior to the present investigation, photometric determinations of copper had been conducted in the presence of iron by using a solution of *pH* greater than 9.0, any nickel present having been removed as nickel glyoxime before formation of the final colour solution. Errors that had previously arisen owing to slight precipitation of the copper diethyldithiocarbamate complex had been eliminated by using larger quantities of gum acacia than those normally employed, and by ensuring that the solution was agitated during the addition of the carbamate reagent. Occasionally, however, considerable difficulty was encountered in obtaining complete removal of nickel from solution, residual quantities of nickel glyoxime precipitating after addition of gum acacia and before the absorption readings had been taken. Further, the presence of dimethylglyoxime frequently caused a brown colour in the test solution that contributed towards erroneous results.

Preliminary experiments failed to provide a satisfactory method for complete precipitation of nickel from solution by means of dimethylglyoxime without deviating considerably from the conditions necessary for the determination of copper. These experiments, however, showed that the foreign brown colour was most probably due to the presence of ferrous dimethylglyoxime complex, the production of which was traced to the action of ultra-violet radiation on solutions containing dimethylglyoxime and ferric citrate. Consequently, the extent of interference from this source was liable to vary with time and with the place in which the test solution had been allowed to stand in the laboratory. The addition of dimethylglyoxime to the blank solution to compensate for the effect of the foreign colour provided a greater degree of accuracy than previously obtained, but did not produce sufficiently satisfactory results.

In view of the unsatisfactory nature of the dimethylglyoxime separation of nickel it was decided that, for the determination of copper in nickel-bearing steels and cast irons, an alternative procedure was necessary. Rather than investigate the use of alternative reagents that might provide a more complete separation of nickel from copper, however, it was considered advisable to endeavour to modify the diethyldithiocarbamate procedure in such a manner as to permit copper determinations to be conducted in the presence of nickel, so avoiding preliminary separations which were liable to introduce errors.

EXPERIMENTAL

EFFECT OF GUM ACACIA ON NICKEL DIETHYLDITHIOCARBAMATE—

In the first instance the effect of larger gum additions on the behaviour of nickel diethyldithiocarbamate was examined by conducting a series of tests with increasing quantities of gum acacia and various percentages of nickel, while otherwise maintaining the conditions of the usual diethyldithiocarbamate procedure. Percentage nickel values were based on the use of a 0.5 g. sample and the subsequent treatment of a 10 ml./100 ml. aliquot portion, prior to dilution to 100 ml. Drum readings were obtained using a 2-cm. cell and spectrum No. 602 blue filters in conjunction with heat-resisting filters H.503.

Since interference was caused by flocculation of colloidal nickel diethyldithiocarbamate,

care was taken throughout these tests to obtain drum readings as soon as possible after formation of the colour solution, so avoiding any possible errors due to variable delay. Results of these tests are shown in Fig. 1.

These results clearly demonstrated the serious nature of nickel interference on determinations of copper. They also indicated that, although increased concentrations of gum acacia decreased nickel interference to some degree, the extent to which this occurred provided no material advantage, particularly when relatively high concentrations of nickel were present. It was also apparent that correction curves to compensate for nickel interference would not serve to provide reproducible results.

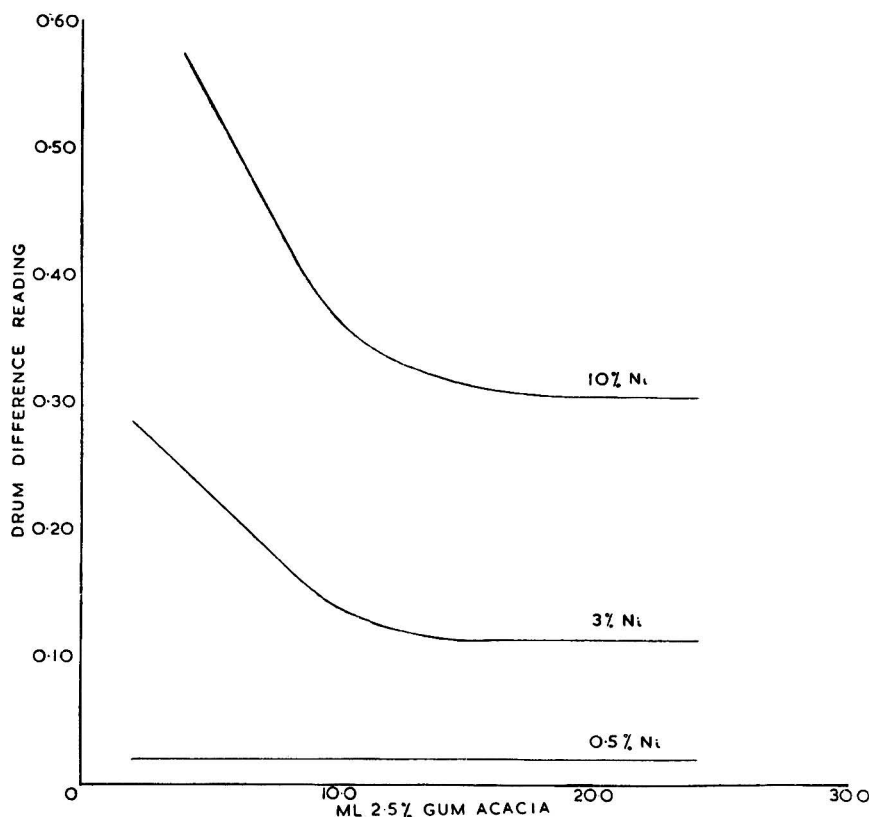


Fig. 1. Effect of gum acacia on nickel diethyldithiocarbamate.

EFFECT OF AMMONIA ON NICKEL DIETHYLDITHIOCARBAMATE—

Some indication had previously been obtained of the soluble nature of the nickel diethyldithiocarbamate complex in ammoniacal solution. A series of tests was conducted, therefore, in which the conditions were similar to those of the earlier tests except that 10 ml. of 2.5 per cent. gum acacia solution were added throughout, and volumes of aqueous ammonia (sp.gr. 0.880) ranging from 2.0 to 30.0 ml. were added; each test solution was finally made up to 100 ml. as before.

In order to ascertain if the time interval between formation and measurement of the colour solution had any significant influence on the accuracy of results, absorption measurements of the test solutions containing 10 per cent. of nickel were obtained again after a period of 3 hours. Results of these tests are shown in Fig. 2.

The presence of excess of ammonia was shown to be ideal for suppression of nickel interference, the quantity necessary being dependent upon the quantity of nickel present.

It was also shown that, provided sufficient ammonia was present, the time interval between formation and measurement of the colour solution was not critical. If, however, insufficient ammonia was present, very serious errors could be introduced.

To obtain more specific information concerning the permissible variation in nickel concentration for any particular concentration of ammonia, five series of tests were conducted, the content of ammonia being maintained constant within each series, while the nickel content varied. The concentrations of aqueous ammonia chosen were 5 ml., 15 ml., 20 ml., 25 ml. and 30 ml. respectively of aqueous ammonia (sp.gr. 0.880) per 100 ml. of solution. Results of these tests are shown in Fig. 3.

These graphs showed that conditions existed whereby nickel interference could be suppressed almost completely and certainly sufficiently for most practical purposes. When

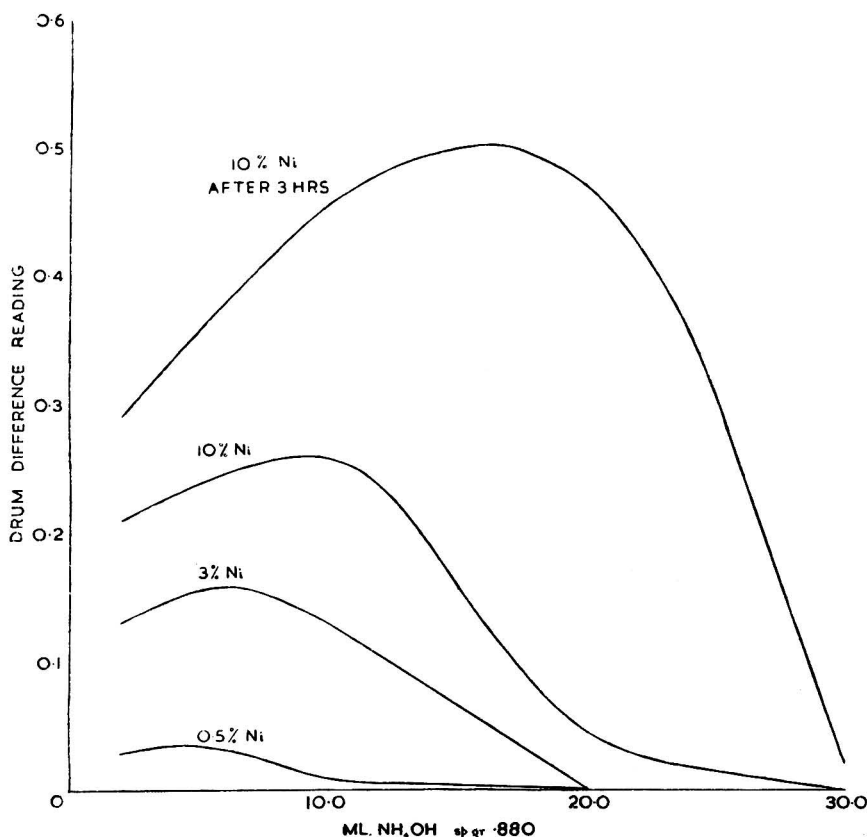


Fig. 2. Effect of ammonia on nickel diethyldithiocarbamate.

dealing with alloys having nickel contents of the order of 10.0 per cent., it was apparent that the use of 30 ml. of aqueous ammonia (sp.gr. 0.880) in the analytical procedure was necessary. In view of this high concentration and the accompanying pungent vapours, it was felt most desirable to have available also a procedure which, by employing a lower concentration of ammonia, would provide an atmosphere more comfortable to the analyst. Results indicated that, to meet these requirements, a concentration of 20.0 ml. of aqueous ammonia (sp.gr. 0.880) per 100 ml. of final solution would be adequate for samples containing up to about 5 per cent. of nickel.

Since it was apparent from information obtained that the minimum concentration of ammonia required would be in excess of that previously used in the original diethyldithiocarbamate procedure, analyses were conducted, prior to the preparation of calibration curves, to ascertain whether the concentration of ammonia present in the modified procedure might be such as to promote crystallisation of ammonium salts, when applied to the analysis of ferrous materials. Trouble in this respect was indeed encountered, and, consequently, it was found necessary to reduce the quantity of acid present in the final aliquot. This was accomplished by increasing the weight of sample, and decreasing the aliquot taken for colour measurement, whilst maintaining the volume of solvent acid previously used.

As a basis for further tests, three calibration curves were prepared, by using (a) 30 ml., (b) 20 ml. and (c) 15 ml. of aqueous ammonia (sp.gr. 0.880). The procedure adopted involved the use of solutions of spectrographically pure iron, to each of which was added different volumes of a standard copper solution. Using these curves, determinations of copper were made on copper-bearing solutions of spectrographically pure iron to which were added

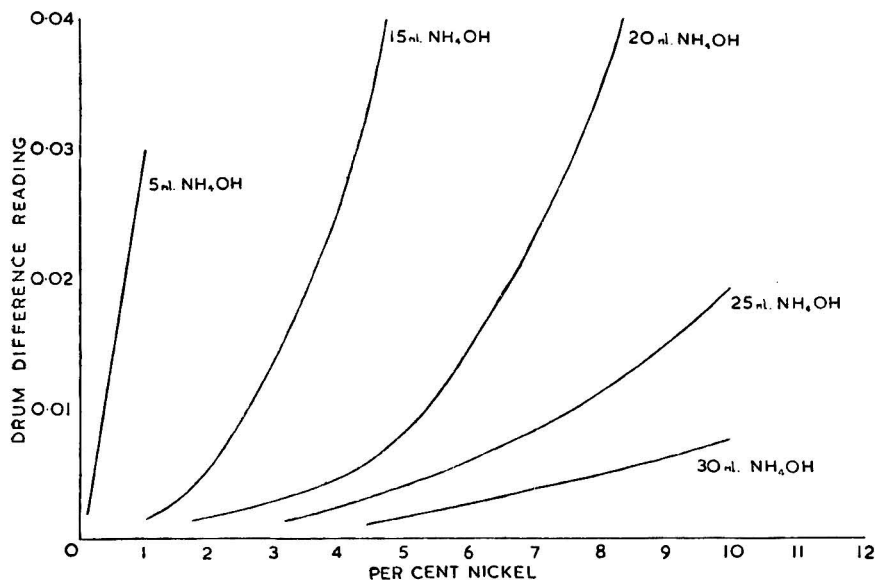


Fig. 3. Nickel interference relative to the concentration of ammonia.

specific volumes of a standard nickel solution. The concentrations were so chosen that each test solution contained an equivalent of 0.5 per cent. of copper, whilst, over the series, the nickel content varied from 0.0 to 10.0 per cent. Percentage figures were based on the use of a 1-g. sample and the subsequent treatment of a 10 ml./200 ml. aliquot portion prior to dilution to 100 ml. Results of these tests are shown in Table I.

TABLE I

EFFECT OF HIGH CONCENTRATIONS OF AMMONIA ON THE SUPPRESSION OF NICKEL INTERFERENCE IN COPPER DETERMINATIONS

Ni added %	Cu added %	Cu found, % (15 ml. conc. aq. NH ₃)	Cu found, % (20 ml. conc. aq. NH ₃)	Cu found, % (30 ml. conc. aq. NH ₃)
0.0	0.500	0.500	0.500	0.500
0.5	0.500	0.500	0.500	0.500
1.0	0.500	0.505	0.500	0.500
2.0	0.500	0.500	0.505	0.500
4.0	0.500	0.515	0.505	0.505
6.0	0.500	0.560	0.540	0.505
8.0	0.500	0.565	0.530	0.505
10.0	0.500	0.555	0.635	0.505

The above figures, recorded to the nearest 0.005 per cent., showed clearly that, for the determination of copper in presence of nickel, using a 1-g. sample, interference due to nickel could be eliminated, for practical purposes, by the use of 15 ml., 20 ml. and 30 ml. of aqueous ammonia (sp.gr. 0.880) for nickel contents of approximately 2.0, 4.0 and 10.0 per cent. respectively.

STABILITY OF COPPER DIETHYLDITHIOCARBAMATE IN PRESENCE OF HIGH CONCENTRATIONS OF AMMONIA—

Using synthetic solutions prepared as described above, but containing 0.75 per cent. of copper, tests on the stability of the final colour produced under the new conditions were

conducted in the presence and absence of nickel. The higher concentration of copper was deemed advisable for this particular series of tests in order that any tendency towards fading of the colour solution might be intensified, and therefore more readily noted. The concentrations of nickel chosen were in each case a maximum for the concentration of ammonia employed. Results of these tests are shown in Table II.

TABLE II

EFFECT OF HIGH CONCENTRATIONS OF AMMONIA ON THE STABILITY OF THE COPPER DIETHYLDITHIOCARBAMATE COLOUR IN PRESENCE AND ABSENCE OF NICKEL

Time interval between colour and absorption measurement *	15 ml. conc. aq. NH ₃ per 100 ml. soln.		20 ml. conc. aq. NH ₃ per 100 ml. soln.		30 ml. conc. aq. NH ₃ per 100 ml. soln.	
	Cu: 0.75% Ni: nil	Cu: 0.75% Ni: 2.00%	Cu: 0.75% Ni: nil	Cu: 0.75% Ni: 4.00%	Cu: 0.75% Ni: nil	Cu: 0.75% Ni: 10.00%
	Cu found %	Cu found %	Cu found %	Cu found %	Cu found %	Cu found %
2 minutes	0.750	0.750	0.745	0.745	0.750	0.750
5 "	0.750	0.750	0.750	0.750	0.750	0.745
10 "	0.750	0.750	0.750	0.745	0.745	0.745
15 "	0.755	0.755	0.750	0.755	0.755	0.750
20 "	0.750	0.755	0.755	0.750	0.755	0.750
25 "	0.755	0.760	0.755	0.755	0.755	0.750
30 "	0.755	0.760	0.755	0.755	0.760	0.755
35 "	0.750	0.765	0.755	0.755	0.760	0.755
40 "	0.750	0.765	0.755	0.755	0.760	0.755
50 "	0.760	0.775	0.765	0.760	0.765	0.765
1 hour	0.760	0.780	0.765	0.760	0.765	0.765
2 hours	0.770	0.920	0.780	0.815	0.780	0.775
3 "	0.775	1.150	0.790	1.080	0.790	0.790

The results indicated that, within reasonable time limits, and in absence of nickel, no serious effect was produced on the colour of copper diethyldithiocarbamate solution by the presence of high concentrations of ammonia.

When dealing with nickel-bearing steels it was apparent that in order to obtain acceptable accuracy the time interval between the formation and measurement of the colour solution should not exceed 30 minutes. In absence of nickel, however, the colour solution remained essentially stable for a period of about 1 hour. It was, of course, clear that to obtain maximum accuracy, measurements should be made as soon as possible after the formation of the colour solution.

It was borne in mind that previous tests had been based on the use of a final sample of 0.05 g. per 100 ml. and that under these conditions a range of copper content of 0.0 to 1.0 per cent. was obtained when using a 2-cm. cell. It appeared reasonable to assume that, by using smaller cells, proportionately higher concentrations of copper might be determined. Experimental tests with concentrations of copper in the range of 1.0 to 2.0 per cent. failed to support this assumption, however, and, indeed, showed it to be invalid owing to the occurrence of turbid solutions caused by breakdown of colloidal copper diethyldithiocarbamate. When dealing with copper contents greater than 1.0 per cent., therefore, the necessity arose to decrease the weight of sample taken rather than to employ the usual weight of sample with smaller cells.

THE METHOD

The method involves solution of the sample in sulphuric-phosphoric acid mixture, oxidation with nitric acid and coloration of an aliquot portion with sodium diethyldithiocarbamate in ammoniacal solution in presence of gum acacia. Metals insoluble in aqueous ammonia are held in solution by means of ammonium citrate, and nickel interference is suppressed by the presence of ammonia.

REAGENTS—

Phosphoric-sulphuric acid—Add 150 ml. of concentrated sulphuric acid and 150 ml. of syrupy phosphoric acid (sp.gr. 1.75) to distilled water and dilute to 1 litre.

Nitric acid—Sp.gr. 1.20.

Ammonium citrate solution—Add 500 ml. of aqueous ammonia (sp.gr. 0.880) to a solution of 500 g. of citric acid in about 200 ml. of distilled water. Dilute to 1 litre with distilled water.

Aqueous ammonia—Sp.gr. 0.880.

Gum acacia solution—Dissolve 12.5 g. of gum acacia in 300 ml. of hot distilled water. Dilute to 500 ml.

Sodium diethyldithiocarbamate solution—Dissolve 0.5 g. in distilled water. Dilute to 250 ml.

Copper—AnalaR copper sheet.

Standard copper solution—Dissolve 0.5 g. of AnalaR copper sheet in a few ml. of nitric acid, boil to expel nitrous fumes and dilute to 1000 ml. with distilled water. Measure off 50 ml. and dilute to 1000 ml. (1 ml. \equiv 0.05 per cent. of copper on a 0.05-g. sample.)

PROCEDURE—

Take 1.0 g. of the sample for alloys containing up to 1.0 per cent. of copper and proportionately less sample for alloys of higher copper contents. Add 20 ml. of phosphoric-sulphuric acid, heat, and when solution is complete, oxidise with 5 ml. of nitric acid. Boil to expel nitrous fumes, filter if necessary, cool, and dilute to 200 ml. Proceed as follows, according to the nickel content of the sample.

Samples containing up to 4.0 per cent. of nickel—

Take two 10-ml. aliquot portions, (a) test solution and (b) compensating solution, and transfer to 100-ml. graduated flasks.

To (a) add 10 ml. of ammonium citrate solution, 20 ml. of aqueous ammonia (sp.gr. 0.880), and 10 ml. of gum acacia solution and dilute to approximately 80 ml. Shake well, add 10 ml. of sodium diethyldithiocarbamate solution and finally dilute to 100 ml. with distilled water. Mix well.

To (b) add 10 ml. of ammonium citrate solution, 20 ml. of the aqueous ammonia and 10 ml. of gum acacia solution and dilute to 100 ml. with distilled water. Mix well.

Within a period of 30 minutes measure the absorption of each of these solutions under the following conditions:—

Instrument setting:	Water/water 1.00
Light source:	Tungsten filament lamp
Filters:	Ilford Spectrum Blue, No. 602, and heat-resisting, H.503
Size of cell:	2 cm. (for 0 to 1.0 per cent. copper) 4 cm. (for 0 to 0.5 per cent. copper)

Samples containing from 4.0 to 10.0 per cent. of nickel—

Proceed as above, but add 30 ml. of the aqueous ammonia in place of 20 ml.

Convert difference readings obtained by either of the above procedures to percentage content by reference to calibration curves prepared as described below.

CALIBRATION—

Treat 1.0 g. of spectrographically pure iron as described in the procedure, measure off a number of 10-ml. aliquot portions, and to these, before addition of ammonium citrate, add volumes of the standard copper solution, varying from 0 to 20 ml. Continue the treatment as described for the test solution and obtain the absorption readings. In order to correct for any copper present in the iron and reagents employed, conduct in the same manner a blank determination on an aliquot portion of solution to which no copper has been added. Plot the differences between the absorptions of each test solution and the absorption of the blank solution against the various percentages of copper added. Prepare two calibration curves employing 20 ml. and 30 ml., respectively, of aqueous ammonia (sp.gr. 0.880).

NOTES ON THE METHOD—

- (i) Since the nature of the colour solution causes staining of the glass cells, these should be cleaned frequently with dilute nitric acid.
- (ii) Since the solutions prepared for absorption measurements contain high concentrations of gum acacia, solid matter dries readily on the outside surfaces of the glass cells. These should, therefore, be carefully examined prior to absorption readings being made.
- (iii) Blank determinations should be conducted with each batch of analyses in order to correct for copper present in reagents.

RESULTS

The above method was applied to determinations of copper in various types of alloy steels and cast irons. Whenever possible standard alloys were used, but in view of the limited number of suitable standard materials available, resort was made also to alloy cast irons normally received for analysis. Since certified analyses of these materials were not available, determinations of copper were made by referee chemical methods, the mean of three determinations being accepted for each sample as a basis for comparison with results obtained by the photometric procedure. Results are given in Table III.

TABLE III

Sample	Weight of sample taken g.	Copper present (based on 1.0-g. sample) %	Nickel present (based on 1.0-g. sample) %	Nickel added %	Total nickel present %	Copper found %	
						Using 20 ml. aq. NH ₃	Using 30 ml. aq. NH ₃
B.C.S. Steel, No. 214	1.00	0.24	0.16	nil	0.16	0.26; 0.26; 0.27	—
B.C.S. Steel, No. 219	1.00	0.15	2.64	nil	2.64	0.18; 0.17; 0.18	—
Amer. Bur. of Stand. Steel, No. 19c	1.00	0.16	0.18	nil	0.18	0.17; 0.16; 0.17	—
Amer. Bur. of Stand. 18/8 Steel, No. 101	1.00	0.055	8.44	nil	8.44	—	0.06; 0.06; 0.05
B.C.S. Alloy	0.10	0.47	1.35	nil	1.35	0.49; 0.48; 0.47	—
Cast iron	0.15	0.71	2.01	nil	2.01	0.71; 0.72; 0.72	—
No. 173	0.20	0.95	2.69	nil	2.69	0.96; 0.93; 0.95	—
Cu-Cr-Mo cast iron	1.00	0.55	trace	2.00	2.00	0.54; 0.54; 0.55	—
				10.00	10.00	—	0.53; 0.53; 0.54
High duty cast iron	1.00	0.82	trace	nil	nil	—	0.84; 0.80; 0.81
				2.00	2.00	0.82; 0.80; 0.83	—
				10.00	10.00	—	0.82; 0.83; 0.81

CONCLUSIONS

1. The method described is applicable to the determination of copper in plain carbon steels, plain cast irons, low alloy steels and irons, and high alloy steels of the 18/8 type.
2. The procedure obviates the necessity of preliminary separation of nickel since interference due to this element can be suppressed for practical purposes by the presence of excess of ammonia, the quantity of ammonia employed being dependent upon the concentration of nickel present in solution.
3. The method provides a colour solution that is stable for a period of 30 to 40 minutes, and suitable for photometric measurement.

SUMMARY

A photometric method for the determination of copper in nickel-bearing steels and cast irons, by means of sodium diethyldithiocarbamate, is described. The procedure makes possible a direct determination of copper without any preliminary separation of either nickel or iron, use being made of the soluble nature of the nickel diethyldithiocarbamate in ammoniacal solution to suppress nickel interference. The effects of additions of gum acacia and aqueous ammonia on the nickel diethyldithiocarbamate and the effect of high concentrations of ammonia on the stability of the copper diethyldithiocarbamate colour solution have been investigated. The procedure provides figures of high accuracy and may readily be employed for batch analysis.

The authors wish to make acknowledgment to the management of the Research Department of Messrs. Babcock & Wilcox Ltd., for permission to publish the above data.

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BABCOCK & WILCOX LIMITED
 RENFREW, SCOTLAND

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The Reaction of Nitrous Acid with Alcoholic Alpha-Naphthylamine Hydrochloride and Its Application to the Absorptiometric Determination of Nitrites

By C. A. PARKER

(1) INTRODUCTION

THE production of azo dyes by the reaction of mixtures of suitable amines with traces of nitrous acid forms the basis of a number of colorimetric methods for the estimation of nitrites.^{1,2,3,4,5,6,7} Of these, one of the most widely used is the well-known reaction employing sulphanilic acid and α -naphthylamine.^{8,9,10,11,12,13} The colour reaction of nitrous acid with an excess of α -naphthylamine in alcoholic hydrochloric acid, which has already been briefly investigated by the author,¹⁴ suggested a ready means of estimating traces of nitrite, which might have certain advantages over the already existing methods. In the previous work the reaction was carried out in 95 per cent. ethyl alcohol, but for the purpose of nitrite estimation an aqueous medium is often more convenient. Preliminary experiments showed, however, that dilution of the alcohol with water produced a profound effect upon the rate of colour development and that virtually no colour was obtained in an entirely aqueous medium. The purpose of the present work was to investigate in detail the effect of variations in the concentrations of alcohol and hydrochloric acid upon the reaction velocity and maximum colour intensity and thus to develop a sensitive and accurate absorptiometric method for the estimation of nitrite.

(2) RECOMMENDED PROCEDURE FOR THE DETERMINATION OF NITRITES

(a) REAGENTS—

α -Naphthylamine—"A.R." quality material recrystallised from boiling light petroleum (b.p. 40° to 60° C.) to give colourless needles.

Hydrochloric acid—"A.R." quality, 10 N; the normality must not deviate from this value by more than ± 10 per cent.; if a greater deviation is found an appropriate adjustment should be made in the volume taken to prepare the mixed reagent.

95 per cent. Alcohol—Redistilled from sodium hydroxide.

Mixed reagent—Dissolve 1.25 g. of α -naphthylamine in 1000 ml. of alcohol. To this solution add 8.8 ml. of hydrochloric acid. The reagent is stable in the absence of air and light.

(b) PREPARATION OF SAMPLE—

If the sample is strongly acid or alkaline it should first be neutralised to methyl orange by titration with sodium hydroxide or hydrochloric acid. For this titration dilute methyl orange solution may be added at the rate of 0.5 ml. of 0.002 per cent. solution per 20 ml. of sample. This will produce a small drum reading on the "Spekker," which will be automatically compensated when the blank is measured.

When very small quantities of nitrite are to be estimated it is desirable to titrate a 20-ml. aliquot of the sample to methyl orange and then to carry out the nitrite determination on a separate 20-ml. aliquot to which has been added the appropriate amount of acid or alkali to give a total volume not exceeding 22 ml.

(c) PROCEDURE—

Pipette a 20-ml. aliquot of the neutral aqueous sample into a 50-ml. calibrated flask. Pipette in 20 ml. of the mixed alcoholic reagent. Mix, allow to stand in the dark for 10 minutes at room temperature and then place in a water-bath at $60^{\circ} \pm 2^{\circ}$ C. for 30 minutes. Cool to 20° C. and make up to the mark with distilled water. Measure the drum reading with the "Spekker," using Ilford Yellow-Green filters No. 605 in conjunction with either the tungsten or mercury lamp, and the appropriate cell thickness to give a drum reading of less than 1.0. Carry out a blank determination using 20 ml. of nitrite-free water containing (if appropriate) 0.5 ml. of 0.002 per cent. methyl orange solution. Multiply the drum difference reading by the factor obtained from a calibration graph prepared by using standard solutions of sodium nitrite, and thus obtain the concentration of nitrite in the sample.

(3) ADVANTAGES OF THE PROPOSED METHOD

The coloured solutions are stable for several days and obey Beer's law exactly. Reproducible straight-line calibration graphs can be obtained with all sizes of Spekker cell and the slopes are directly proportional to cell thickness. Relatively high or very low concentrations of nitrite may thus be estimated with equal accuracy and without precipitation of the dye. After selection of a suitable cell thickness, drum readings may be converted directly to nitrite concentration by means of the appropriate factor without reference to the calibration curves. In contrast to this, the α -naphthylamine-sulphanilic acid reaction, when carried out in an aqueous medium, gives precipitation of the dye except with very low nitrite concentrations.¹³ It was in an attempt to overcome this difficulty that Richardson and Hollings¹⁰ recommended the use of methylated spirit.

The sensitivity of the reaction is such that, with a 4-cm. cell, less than 1 part of nitrite in 200 million may be detected. The method has the further advantage that the absorption takes place at the wavelength of green light and interference by faint yellows or browns in the solution is minimised. Such interference is generally negligible, but if the sample is strongly coloured accurate compensation may be made by deducting the absorption shown by a solution derived from a similar aliquot of the sample to which has been added alcoholic hydrochloric acid but no α -naphthylamine.

The absorption band of 4-amino-1 : 1'-azonaphthalene hydrochloride (peak at 5500 Å.) is ideally situated for measurements with the 5461 Å. mercury line. This line may be readily isolated by means of the Ilford Yellow-Green filter No. 605. Calibration graphs obtained in this way correspond almost exactly to peak extinction and have slightly greater slopes than those obtained with the tungsten lamp.

(4) EFFECT OF VARIOUS FACTORS UPON THE RATE OF COLOUR DEVELOPMENT

Measurements of reaction velocity were made in the first place at 20° C., with the Spekker photo-electric absorptiometer, using "tall-form" 1-cm. cells which were maintained at constant temperature by means of a specially constructed bath.¹⁵ The procedure used was as follows.

The requisite quantity of a standard alcoholic solution of sodium nitrite (containing from 0.15 to 0.5 mg. of NaNO_2 in 90.0 per cent. w/w alcohol) was placed in a 100-ml. calibrated flask together with the appropriate quantity of water and the volume made up to 79 ml. with 90.0 per cent. w/w alcohol. The flask and contents were brought to the required temperature in a thermostat. A mixed reagent of α -naphthylamine (50 mg. per 20 ml.) and hydrochloric acid (of appropriate concentration) in 90.0 per cent. w/w alcohol was also adjusted in temperature. Twenty ml. of the mixed reagent were then pipetted rapidly into the nitrite solution. The volume was made up to 100 ml. with 90.0 per cent. w/w alcohol and after complete mixing a quantity was poured into one of the dry Spekker cells in the constant-temperature bath. Drum readings (water to water = 1.00) were taken at short intervals of time until the colour was fully developed.

The reaction velocity constant was calculated as follows. First, the drum readings were plotted against time and a mean reaction - time curve drawn (in this way the random errors of the single Spekker measurements were eliminated). Then, assuming that at any

stage of the reaction the colour intensity (*i.e.*, $1 - D_n$) is proportional to the quantity of nitrite that has reacted, the following equation for a first-order reaction applies:

$$\log_{10}(D_n - D_{n'}) = \frac{-kt_n}{2.303} + \log_{10}[(1 - D_\infty)(1 - e^{-kT})]$$

where D_n = drum reading obtained at time t_n .
 $D_{n'}$ = drum reading obtained at time $t_{n'}$.
 D_∞ = drum reading corresponding to infinite time.
 k = first order reaction velocity constant.
 T = an arbitrary and constant time interval.

From the graph of D_n against t_n , values of $\log_{10}(D_n - D_{n'})$ were calculated and plotted against t_n . From the slope of the straight line so obtained the reaction velocity constant was calculated.

α -Naphthylamine was always present in large excess and the reaction was found to be of the first order with respect to the nitrous acid. The reaction velocity constant was first measured in 90.0 per cent. w/w alcohol containing various concentrations of hydrochloric acid. These experiments were then repeated with different concentrations of alcohol. The complete set of results is shown in Fig. 1 (curves 1, 2, 3, 4 and 5). It will be noted that in 90 per cent. w/w alcohol the reaction rate is a maximum at an acid normality of 0.08 (curve 1). It decreases rapidly with decrease of acidity below this point, and more slowly with increase of acidity above this point. On decreasing the concentration of alcohol all the reaction rates are decreased, and at the same time the normality corresponding to maximum velocity moves to lower values, until finally at an alcohol content of 24 per cent. w/w no maximum appears above a normality of 0.02. The theoretical significance of all these effects is discussed in the following section.

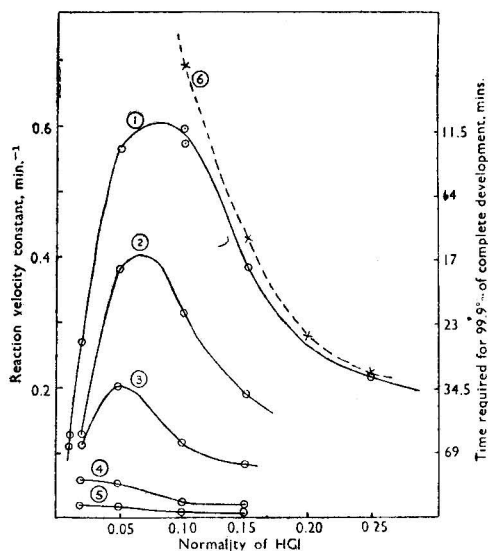


Fig. 1. Effect of concentration of hydrochloric acid and alcohol upon the rate of reaction of nitrous acid with α -naphthylamine at 20° C.

Curve (1) in 90.0% w/w ethyl alcohol.
 " (2) in 61.1% " " "
 " (3) in 50.3% " " "
 " (4) in 32.6% " " "
 " (5) in 23.9% " " "
 " (6) Rate of coupling of α -naphthylamine diazonium chloride with a large excess of α -naphthylamine in 90% w/w ethyl alcohol.

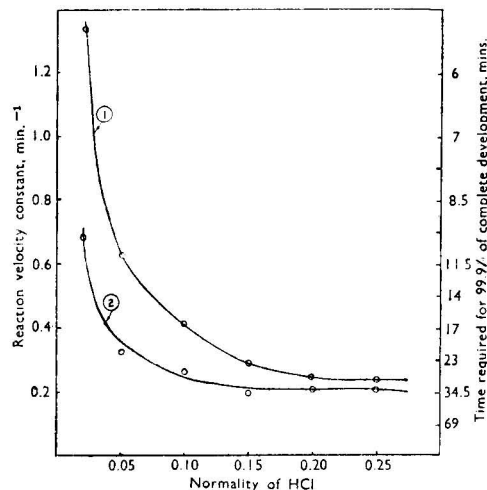


Fig. 2. Effect of concentration of hydrochloric acid and alcohol upon the rate of reaction of nitrous acid with α -naphthylamine at 60° C.

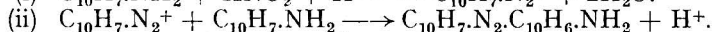
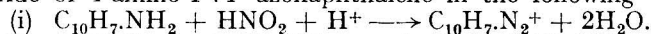
Curve (1) in 32.6% w/w ethyl alcohol.
 " (2) in 23.9% " " "

From the point of view of an analytical method for the estimation of nitrous acid, a compromise has to be made between high rate of development on the one hand and low alcohol concentration on the other. With high water content at 20° C. the reaction is too

slow for convenience. However, 60° C. appears to be a convenient temperature for the test, and reaction velocity experiments at this temperature showed that the colour is fully developed within 30 minutes, even in solutions containing as little as 24 per cent. of alcohol and at fairly high acidities (see Fig. 2). The further investigations, described in sections (6) to (9) below, were therefore confined to 60° C.

(5) DISCUSSION OF THE MECHANISM OF THE REACTION

It has been shown¹⁴ that the colour is due to the formation of the blue-violet hydrochloride of 4-amino-1 : 1'-azonaphthalene in the following way:—



The results described in section (4) above may be explained on the basis of this two-stage reaction. At high acidities the initial diazotisation of the α -naphthylamine is very rapid and the subsequent coupling of the diazonium chloride with a further molecule of α -naphthylamine is the rate-determining step, the rate of coupling being retarded by increase of acidity. On the other hand, at very low acidities, the coupling reaction is very rapid, the diazotisation being retarded and becoming the rate-determining step. This theory has been confirmed by measuring the rate of coupling at varying acidities in the following way—

6.2 mg. (1.2 mol.) of α -naphthylamine in 5 ml. of 0.2 N hydrochloric acid were treated with 5 ml. of an aqueous solution of 2.5 mg. (1 mol.) of sodium nitrite. After 10 minutes standing at room temperature the diazotisation was complete. 1 ml. of the resulting naphthalene diazonium chloride solution was added to a 100-ml. calibrated flask containing 50 mg. of α -naphthylamine in solution in 91 per cent. w/w alcohol containing the appropriate concentration of hydrochloric acid, the latter solution having previously been brought to 20° C. in a thermostat. The mixture was rapidly made up to the mark with 91 per cent. w/w alcohol, mixed, and poured into a dry Spekker cell in the constant-temperature bath. Drum readings were taken at frequent intervals and the reaction velocity constant calculated by the method already described.

Below a normality of 0.10 in 90 per cent. alcohol the rate of coupling increases very rapidly (see Fig. 1, curve 6), but at normalities greater than 0.20 the rate of coupling approximates to the over-all reaction rate.

The reduction of the over-all reaction velocity with decrease of alcohol content, and the accompanying movement of the peak in the curves towards lower acidities (see Fig. 1) suggests an increase in the ionisation of the hydrochloric acid at the lower alcohol concentrations. This would, of course, have the effect of lowering the rate of coupling until finally this reaction would become the rate-determining step throughout the range of acidity investigated.

The rates of coupling of diazonium salts with tertiary amines have been investigated by Goldschmidt¹⁶ who noted a retardation of the reaction on increasing the acidity. Similar effects have been observed by other workers in the reaction of nitrous acid with a mixture of sulphanilic acid and α -naphthylamine. Thus, Moffit¹¹ recommends diazotisation of sulphanilic acid in dilute sulphuric acid solution followed by buffering with sodium acetate to allow the coupling reaction with α -naphthylamine to take place.

Rider and Mellon¹³ have shown that the order of addition of the reagents in this reaction is of great importance: if the α -naphthylamine is added before completion of the diazotisation of the sulphanilic acid, low colour intensities are obtained owing to partial diazotisation of the α -naphthylamine. They recommend preliminary reaction of the sulphanilic acid in acid solution followed by the addition of α -naphthylamine and subsequent buffering with sodium acetate to facilitate the coupling reaction. The application of a similar principle was attempted in the present investigation, acid alcoholic α -naphthylamine solution being added to the nitrite solution followed by sodium acetate to allow coupling to give the brown azo-base. While some success was attained with this procedure, it was felt that the method now recommended had the advantage of simplicity and reproducibility.

(6) EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID UPON THE INTENSITY OF THE FULLY DEVELOPED COLOUR

4-Amino-1 : 1'-azonaphthalene is a weak base and has indicator properties, being red-brown in neutral or alkaline solution and blue-violet in acid solution. The absorption spectrum of the free base exhibits a maximum at 4650 A. in neutral or alkaline alcoholic solution, whilst in strongly acid solution a peak appears at 5500 A. owing to the cation of the basic salt (see Fig. 3). However, the basicity of the compound is so small that appreciable

hydrolysis of the hydrochloride is apparent even in 0.1 *N* alcoholic hydrochloric acid. Consequently the intensity of the peak at 5500 Å. and the Spekker reading obtained with the yellow-green filters (Fig. 4, curve 2) varies with the acid concentration.

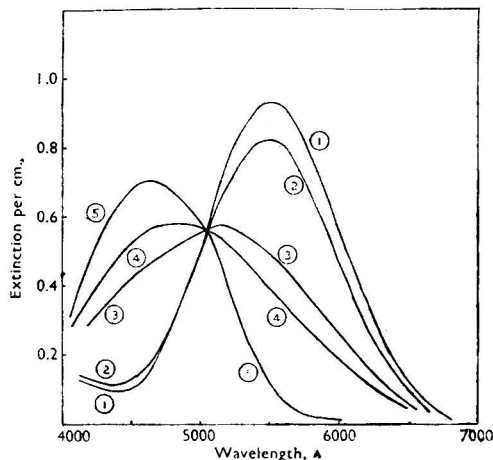


Fig. 3. Effect of acidity upon the absorption spectrum of 4-amino-1:1'-azonaphthalene in 90% alcohol.

- Curve (1) 1 *N* HCl
 " (2) 0.2 *N* HCl
 " (3) 0.01 *N* HCl
 " (4) 0.005 *N* HCl
 " (5) 0.1 *N* NH₄OH

All solutions contain 0.00093% of dye.

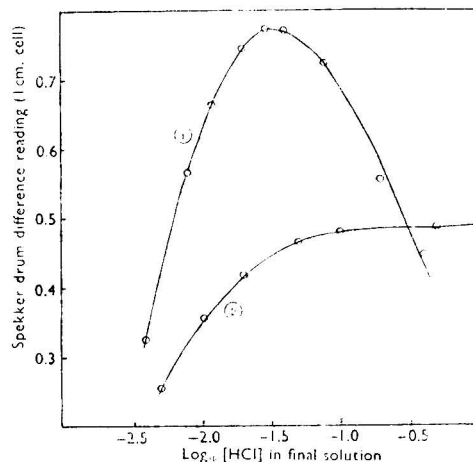
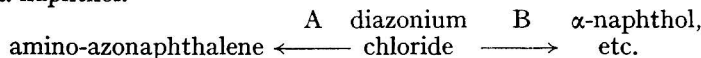


Fig. 4. Effect of concentration of hydrochloric acid upon colour intensity developed from sodium nitrite.

- Curve (1) 0.15 mg. of sodium nitrite treated by prescribed method with mixed reagents containing the appropriate concentration of HCl.

- " (2) 0.0005% solutions of pure 4-amino-1:1'-azonaphthalene in 33% w/w alcohol containing the stated concentrations of HCl.

Solutions obtained by the treatment at 60° C. of sodium nitrite with α -naphthylamine in varying acid concentrations (in a mixture of equal volumes of 95 per cent. alcohol and water—see "Procedure for Determination of Nitrites") show a further effect (Fig. 4, curve 1). At low acidities the extinction, as measured on the Spekker, falls owing to the shift in the absorption band of the dye, but at high acidities the extinction also decreases. A similar effect is shown when the reaction is carried out at 20° C. in those cases where the velocity of the coupling reaction is small (*i.e.*, at low alcohol concentrations). It may be explained by assuming the naphthalene diazonium chloride to undergo two simultaneous reactions, namely, the coupling reaction to give the dye and a decomposition to give colourless products such as α -naphthol.



If reaction A is slow, the effect of B becomes appreciable and low colour intensities are obtained.

The optimum point corresponds to a final normality of 0.03 to 0.04. A normality of 0.035 has been provided for in the recommended method.

(7) EFFECT OF CONCENTRATION OF ALCOHOL UPON THE INTENSITY OF THE FULLY DEVELOPED COLOUR

Fixed amounts of nitrite were treated by the recommended procedure except that different varying amounts of alcohol were used. The results are shown in the following table.

Percentage by volume of "95 per cent. alcohol" in the reaction mixture	"Spekker" drum divisions
30	0.60
35	0.68
40	0.72
45	0.745
50	0.75
60	0.745
70	0.755

For solutions containing less than 50 per cent. by volume of 95 per cent. alcohol the concentration becomes critical and low colour intensities are obtained. A mixture of equal volumes of 95 per cent. alcohol and water was therefore chosen as the reaction medium in the recommended method. After final dilution to 50 ml. with water this corresponds to from 33 to 34 per cent. w/w of alcohol.

(8) EFFECT OF TIME OF STANDING AT ROOM TEMPERATURE BEFORE HEATING TO 60° C.

It was thought possible that reaction at 60° C. might cause abnormally low colour development owing to acceleration of the decomposition of the naphthalene diazonium chloride to colourless products. Since, with the chosen concentrations of reagents, the transformation of nitrous acid to dye is more than 50 per cent. complete within 10 minutes at 20° C., it was decided to allow the solutions to stand for this period at room temperature before completing the reaction at 60° C. The decomposition of the diazonium chloride was thus minimised and a source of variation in the results was removed. Prolonged standing at room temperature before development at 60° C. produced only a slight increase in colour intensity. After heating at 60° C. the solutions were found to be stable for several days when stored in the dark at room temperature; but a gradual fading occurred later.

(9) INTERFERING IONS

The effect of the presence of a number of common ions was investigated, using nitrite concentrations of 0.3 p.p.m. (with 4-cm. cell) and 2.0 p.p.m. (with 1-cm. cell). The salts investigated have been grouped below according to the concentrations that produce an error of less than 5 per cent. in the determination.

10,000 <i>p.p.m.</i>	NaCl, NaNO ₃ , Na ₂ CO ₃ , NaBr, NaC ₂ H ₃ O ₂ . MgCl ₂ , CaCl ₂ , BaCl ₂ , NH ₄ Cl.
1000 <i>p.p.m.</i>	Na ₂ SO ₄ , Na ₂ B ₄ O ₇ , NaH ₂ PO ₄ , Na ₂ SiO ₃ . MnSO ₄ , Co(NO ₃) ₂ , NiSO ₄ , Cr ₂ (SO ₄) ₃ , ZnSO ₄ , Pb(NO ₃) ₂ .
100 <i>p.p.m.</i>	NaF, Na ₂ SO ₃ .
10 <i>p.p.m.</i>	FeCl ₂ , FeCl ₃ , CuSO ₄ .
<10 <i>p.p.m.</i>	Na ₂ S.

Alkalis and alkaline earth metals and nitrate ion are without effect even in concentrations as high as 1 per cent. High concentrations of chloride cause a slight increase in the colour intensity; a similar effect has been noted by Morpeth¹² with the α -naphthylamine - sulphanilic acid reaction. Sulphates in very high concentration cause a considerable diminution in the Spekker reading owing to the suppression of the formation of the hydrochloride of the dye (the solutions having a reddish tint).

Large quantities of basic salts will, of course, interfere with the test, either by completely inhibiting the formation of the dye, or by decreasing the formation of its hydrochloride. These effects are minimised in the proposed method by first neutralising the solution to methyl orange, the small absorption due to the latter being deducted from the drum reading obtained. When very low concentrations of nitrite are concerned the titration may be carried out on a separate aliquot and the requisite volume of hydrochloric acid added to the sample before development of the colour. Generally speaking, however, this neutralisation will be unnecessary.

Interference caused by inert coloured ions may, of course, be automatically compensated by carrying out a blank determination omitting only the α -naphthylamine. Certain ions (notably Fe⁺⁺⁺) produce a precipitate with the reagent, and their concentrations must therefore be kept within low limits.

When estimations of nitrite are required in presence of high concentrations of ions such as sulphate or phosphate, which change the tint of the dye, accurate results may be obtained by preparing a fresh calibration curve relating to the appropriate quantity of interfering ion present.

SUMMARY

A detailed study has been made of the colorimetric reaction between nitrous acid and an aqueous-alcoholic solution of α -naphthylamine hydrochloride. The effects of acid normality, alcohol concentration and temperature upon the reaction velocity and maximum colour

intensity are described, and some observations have been made concerning the mechanism of the reaction.

As a result of these investigations a sensitive and accurate absorptiometric method for the estimation of nitrite has been developed. It has the advantages of rapidity, colour stability and reproducibility. Few ions interfere seriously and the dye obeys Beer's law over a wide concentration range.

The investigations described above were carried out at the Admiralty Materials Laboratory and permission to publish this paper is gratefully acknowledged. The author wishes also to acknowledge the valuable assistance given by Mr. A. P. Goddard with the experimental work.

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ADMIRALTY MATERIALS LABORATORY
HOLTON HEATH, POOLE, DORSET

March, 1948

The Determination of Poisonous Metals (Copper, Lead and Zinc) in Edible Gelatin

By A. SCOTT-DODD

THE Edible Gelatin (Control) Order, 1947, No. 161, January 30th, 1947, fixed the following limits for poisonous metals—

Copper	30	parts per million
Lead	10	" "
Zinc	100	" "

The chief source of trouble in testing gelatin is the viscous nature of its solutions. Hydrolysis with hydrochloric acid and water removes this difficulty and at the same time precipitates some of the proteid matter. After filtration from this it is found that all the metallic impurities are present in the filtrate. A small amount of iron is usually present, and must either be removed or kept from interfering with the subsequent reactions. It is found that, from an aqueous solution acidified with hydrochloric acid, all the copper and iron are extracted by a solution of dithizone in chloroform. It is a simple matter to separate the iron from the copper by precipitation with ammonia, leaving the copper salts in solution. As the contents of the separator now contain only the zinc and lead, these metals are readily extracted by dithizone after a slight excess of ammonia has been added. It is easy to determine the quantity of each, as there should be neither copper nor iron present to interfere with the reactions of potassium ferrocyanide or sodium sulphide. As a precaution, however, it is advisable to add some potassium cyanide, when testing for lead with sodium sulphide.

The details of the method are as follows.

METHOD

REAGENTS—

Solution of diphenylthiocarbazone (dithizone) in chloroform, 0.1 per cent.

Solution of sodium diethyldithiocarbamate, 0.1 per cent. in water.

Solution of potassium ferrocyanide, 1 per cent.

Solution of potassium cyanide, 10 per cent.

Solution of sodium sulphide, 1 per cent.

Standard solutions of copper, zinc and lead, prepared as below.

Copper standard—Dissolve 0.7856 g. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in distilled water, add a few drops of concentrated sulphuric acid and make up to a litre. Dilute ten-fold with distilled water. This makes a standard solution containing 0.02 g. of Cu per litre.

Zinc standard—Dissolve 0.220 g. of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water and make up to a litre. This makes a standard solution containing 0.05 g. of Zn per litre.

Lead standard—Dissolve 0.3662 g. of lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ in distilled water, add a few drops of acetic acid and make up to a litre. Dilute this solution 100-fold with distilled water. This makes a standard solution containing 0.01 g. of Pb per litre.

PROCEDURE—

To 25 g. of gelatin add 10 ml. of concentrated hydrochloric acid and 100 ml. of water, digest on a steam-bath for one day and overnight, in a conical flask. Cool and make up to 250 ml. Filter this 10 per cent. stock solution as required.

Extract 60 ml. of the filtrate (equal to 6 g. of sample) in a separator with about 5 ml. of dithizone reagent, four times.

Collect the extract in a small "CO₂ flask" and distil off the chloroform in a Soxhlet tube. Transfer to a platinum basin, by washing out with small successive quantities of chloroform, and ignite gently with the aid of a few drops of concentrated sulphuric acid and a few drops of nitric acid until all the organic matter and nitric acid disappears. Heat to boiling with water and a few drops of hydrochloric acid, cool and make up to 50 ml. (Solution A.)

Copper—Take 25 ml. of solution A (equal to 3 g. of sample), add a distinct excess of ammonia solution, heat, filter through a small filter paper and wash into a Nessler tube to remove any iron that may be present. Add 2 ml. of 0.1 per cent. sodium diethyldithiocarbamate solution, and compare with the standard copper solution (0.02 g. per litre); 3 ml. of this standard solution \equiv 20 parts of copper per million of the sample.

Zinc and lead—To the contents of the separator add ammonia solution to slight alkalinity. Extract four or five times with 5 ml. of dithizone reagent. Treat the extract as above and make up, as before, to 50 ml. (Solution B.)

Zinc—To 25 ml. of solution B (equal to 3 g. of sample) add a few drops of hydrochloric acid, 1 g. of ammonium chloride and 1 drop of potassium ferrocyanide solution. Compare with the standard zinc solution (0.05 g. per litre); 3 ml. of this standard solution \equiv 50 parts of Zn per million of the sample.

Lead—To 25 ml. of solution B and 1 g. of ammonium acetate, with sufficient ammonia to make the solution distinctly alkaline, add 1 ml. of 10 per cent. potassium cyanide solution and then 1 ml. of 1 per cent. sodium sulphide solution. Compare with the standard lead solution (0.01 g. of Pb per litre); 3 ml. of this standard solution \equiv 10 parts of Pb per million of the sample.

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June, 1947

Notes

THE ESTIMATION OF SELENIUM IN LEAD ALLOYS*

SELENIUM in small amounts is now sometimes added to lead alloys as a grain refiner, and the following method for its determination has been found to give good results. The alloy, preferably in the form of filings or very small pieces, is dissolved in perchloric acid and diluted to a suitable volume with diluted hydrochloric acid (1 + 2). Sulphur dioxide is passed into the solution and causes precipitation of the selenium as a scarlet precipitate. The selenium is filtered off, washed free from lead salts and determined according to the method of B. S. Evans (*Analyst*, 1942, **67**, 88).

Method—

Dissolve 3 g. of the alloy in 30 ml. of perchloric acid (which has previously been concentrated by evaporation to strong fuming) and warm until all action ceases. Heat until all black particles have dissolved. Cool, add 400 ml. of diluted hydrochloric acid (133 ml. of the concentrated acid plus 267 ml. of water) and boil until all salts have dissolved and the solution is quite clear. While the solution is still hot pass in a brisk stream of sulphur dioxide for 3 or 4 minutes to precipitate the selenium, and tellurium if present. Place on the hot-plate for $\frac{1}{2}$ hour, then filter on pulp, keeping the solution hot in order to avoid, as far as possible, the separation of lead chloride. Wash thoroughly with boiling hot diluted hydrochloric acid (1 in 20) until the pulp and precipitate are free from lead salts; 200 ml. or more will be required. From now on, the process is as described by B. S. Evans, *i.e.*, the precipitate is dissolved from the filter by means of bromine solution in dilute hydrochloric acid (5 ml. of a saturated solution of bromine in concentrated hydrochloric acid + 10 ml. of water), the solution being collected in a flask, and the filter is washed with 5 per cent. hydrochloric acid solution so that finally 100 to 150 ml. of filtrate coloured deep orange with bromine are obtained; the filter should be white. Remove excess of bromine from the solution by bubbling through it a rapid stream of air until the colour is pale lemon-yellow. Next add 20 ml. of 4 per cent. potassium iodide solution and shake well. Leave for 1 to $1\frac{1}{2}$ hours with occasional shaking, filter off the scarlet precipitate on a pulp filter and wash (a) with 100 ml. of a solution containing 5 per cent. of hydrogen chloride and 5 per cent. of ammonium chloride, (b) twice with 5 per cent. ammonium chloride solution to remove excess of acid and (c) five or six times with 5 per cent. ammonium nitrate solution to remove chlorides. Suck the washed filter (with selenium precipitate) dry by momentarily attaching the stem of the funnel to a filter pump, blow it out into a beaker, wiping the funnel with a piece of moist filter paper, run 10 ml. of 10 per cent. potassium cyanide solution over the walls of the funnel into the beaker and rinse with hot water. Add sufficient water to enable the paper pulp in the beaker to be disintegrated with a glass rod, stir in 0.4 g. of sodium nitrite and place in a steam-bath. After solution of the precipitate run in 25 ml. of nitric acid (sp.gr. 1.2), stir thoroughly and heat to boiling. Filter into an Erlenmeyer flask of about 600-ml. capacity, wash the pulp thoroughly with hot water and discard it. Evaporate the solution to about 40 ml., cool and roughly measure its volume, place 1 g. of urea in the Erlenmeyer flask, pour the solution back into that flask and rinse the measuring tube with cold water into the flask so as to give a total volume of 100 ml. Add 2 ml. of 10 per cent. potassium cobaltcyanide solution in case a trace of copper has found its way into the solution. Shake, leave for about 1 minute, add 10 ml. of 4 per cent. potassium iodide solution and 5 ml. of chloroform and shake thoroughly again. Leave for 5 minutes with repeated shakings and titrate the liberated iodine with 0.01 N sodium thiosulphate, with vigorous shaking near the end, and using starch for the final end-point. The end-point is orange, owing to precipitated selenium, which accumulates in the chloroform.

Factor: 1 ml. of 0.001 N sodium thiosulphate \equiv 0.0001975 g. selenium.

The following results were obtained with samples of lead alloy containing 3 per cent. of tin and 3 per cent. of antimony to which selenium had been added.

Alloy taken	Selenium added g.	Titration ml.	Selenium found g.	Selenium	
				added % of alloy	found % of alloy
3.0	0.0009	4.8	0.00095	0.030	0.031
3.0 †	0.0006	3.1	0.00061	0.020	0.020
3.0	0.0024	12.1	0.00239	0.080	0.080

The method is unsuitable for alloys containing higher percentages of tin, owing to the formation of insoluble metastannic acid during solution in the perchloric acid.

Thanks are due to the Chief Scientist, Ministry of Supply, for permission to publish this note.

F. W. Box

July, 1948.

A TRANSMITTING MANOMETER FOR MICRO OXYGEN UPTAKE EXPERIMENTS

APPARATUS for the measurement of the oxygen uptake of oils and fats has been extensively studied.^{1,2} On attempting to perform the measurement on a micro-scale, the capacity of the indicating manometer

* Communication from the Armament Research Department (formerly Research Department, Woolwich).

† This alloy contained also 0.02% of tellurium and 0.02% of arsenic.

is no longer negligible in relation to that of the remainder of the system, and it becomes desirable to enclose the entire system in a constant-temperature oven.³ Under these conditions an indirect method of reading the manometer is necessary. An electrical method was accordingly developed, the connecting wires entering the oven through the thermometer aperture.

The construction of the manometer U-tube is shown in Fig. 1. To the platinum contacts A A are attached filaments B B of 36 S.W.G. platinum wire. The ends of the latter are sealed into the glass at the bend of the tube, so that the filaments are under very light tension and are central in the limbs. A third contact, C, sealed through the glass, enables electrical contact to be made with the mercury, which is introduced to a level about half-way up the limbs. One of the side-tubes is connected to the absorption vessel, the other being left open to the atmosphere. (If the manometer is to be used differentially, appropriate connections are made to both side-tubes.)

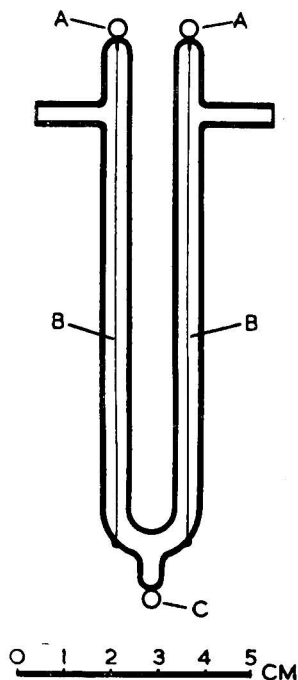


Fig. 1.

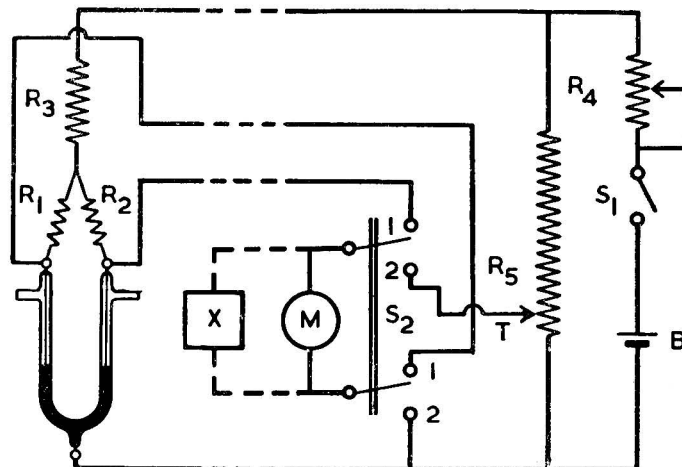


Fig. 2.

R_1 and R_2 , equal, about 1.5 ohms.

R_3 , 13 ohms.

R_4 , 10 ohms.

R_5 , 200 ohms.

M, Galvanometer.

S_1 , On-off switch.

S_2 , Double-pole double-throw switch.

X, Recorder.

Electrical connections are shown in Fig. 2. The filaments, together with resistances R_1 and R_2 , constitute a Wheatstone network, the state of balance of which is indicated by meter M. Pressure changes displace the mercury column, thereby altering the relative effective lengths of the filaments in the circuit and consequently altering the state of balance. The meter is calibrated against a series of known pressure differences. Resistance R_3 limits the potential drop across the network to about 0.4 volt, thus avoiding heating effects.

In order to maintain the calibration the voltage applied to the network must be constant. The applied voltage may be adjusted or checked by moving switch S_2 from position 1 to position 2 and adjusting variable resistance R_4 until the meter gives a full-scale or other convenient predetermined reading. The position of tap T near one end of resistance R_5 is adjusted to suit the particular meter in use. Except for R_4 , which is a radio component, all resistances are made from 35 S.W.G. Eureka wire. In no case is the value critical.

Results obtained using a Griffin & Tatlock "Microid" central zero galvanometer (1.6 microamperes per scale division) are shown in Fig. 3. Pressures were measured on a water manometer and converted into millimetres of mercury. In the range shown, indications of pressure change were instantaneous and reproducible. Use of a Cambridge "Spot" galvanometer (full-scale deflection, approx. 1 microampere) equipped with a suitable shunt enabled the sensitivity to be increased. With pressure differences less than about 4 mm. of mercury, results were somewhat erratic, presumably owing to slight sticking of the mercury. If it is desired to operate at such low pressures the difficulty can be overcome by mounting the manometer on an upright to which a buzzer operated by two dry cells is also attached. The slight agitation thus produced causes the mercury level, and hence the meter reading, to respond instantly to small pressure changes. A typical calibration curve thus obtained is shown in Fig. 4.

The apparatus is obviously of general application to other cases involving pressure indication, e.g., measurement of gas flow or gas thermometry. Not only can readings be obtained at a distance, but it should be possible also to replace meter M by a recorder, so that results may be studied at leisure.

Subsequent to the completion of this work, our attention was drawn to a paper,⁴ describing a manometer device operating a recorder through a Wheatstone network, but using an entirely different principle. A platinum filament, electrically maintained at a slightly elevated temperature, extends down one limb of the manometer U-tube, in which a paraffin filling is used. Movement of the paraffin level alters the immersion, and hence the cooling, of the filament. Change in resistance thus caused alters the state of the bridge balance. This device is very sensitive, but fluctuations in the heating current must be carefully avoided.

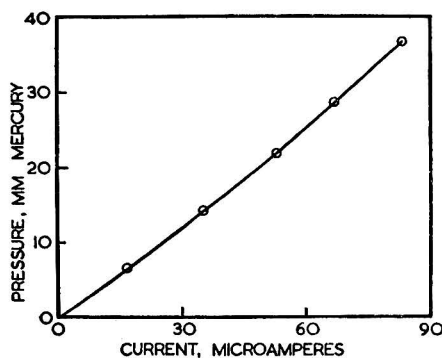


Fig. 3.

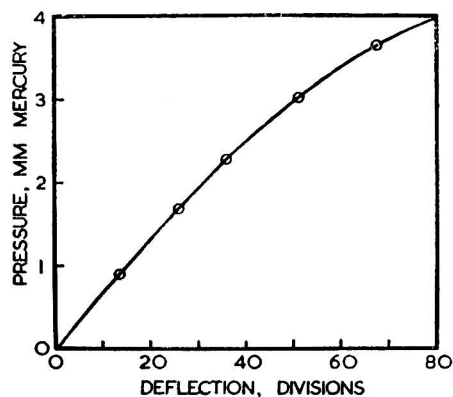


Fig. 4.

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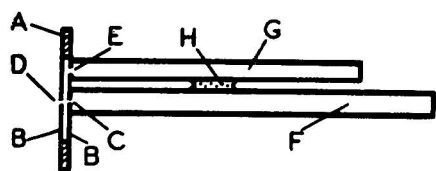
A MICRO-BLOWPIPE

THE apparatus described provides a small, stable, hot flame suited to the fabrication of micro-balance beams, micro-dispensing and drop testing devices, and the like, from capillaries and fine glass rod.^{1,2,3} The cost is negligible and the air supply may be provided by a device operating from a filter pump.

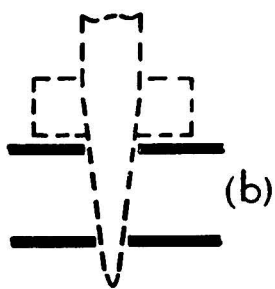
Details of construction are shown in Fig. 1. The gas chamber consists of a steel washer A ($1\frac{1}{8}$ inch outside diameter \times $\frac{13}{16}$ inch inside diameter \times 16 S.W.G.), on the opposite faces of which are soldered discs B of copper foil approximately 0.1 mm. thick, as shown in section at (a). The centre of one of the discs having been marked by an ink dot, the gas chamber is placed on a block of wood and, by careful tapping, a No. 7 sewing needle is driven squarely through the centres of both discs, so that the point of the needle emerges about 1 mm. from the lower disc, as shown diagrammatically at (b). A collar of cork on the needle is useful as an indicator of the correct penetration. The smaller hole, C, is the air jet, the flame issuing from the larger hole D. Gas enters the chamber through hole E, which is about 2 mm. in diameter. To permit attachment of the gas and air lines, two pieces of thin-walled brass tubing F and G (cut from old cork-boreis) are soldered to the lower disc as shown, care being taken not to fill up the holes. A bridge of solder H, towards the lower ends of the tubes, renders the assembly completely rigid.

The modification shown in Fig. 2 is for use in the hand instead of in a retort clamp. The gas chamber is formed by bending one end of a length of $\frac{1}{8}$ -inch outside-diameter copper or brass tubing into a flat loop, as shown at (a). Ports A A, for gas entry, are filed, and the chamber is closed by soldering suitably shaped pieces of copper foil to the opposite faces of the loop, as shown in section at (b). Holes are pierced through the foils as before and a short length of thin-walled brass tubing B is soldered to the rear of the chamber to allow connection of the air tube. A second length of $\frac{1}{8}$ -inch outside diameter tubing C, bent as shown, is secured to the gas tube D by two bridges of solder. The upper end of C is connected to B by a short length of cycle valve tubing E. A hook, F, of brass wire enables the blowpipe to be hung up when desired.

The filter-pump-operated device shown in Fig. 3 is a convenient means of producing the necessary air blast. Its construction and principles of operation are similar to those of the stirrer unit previously described.⁴ It is, however, larger, and the valve rod has at its lower end a rubber buffer A, of cycle valve tubing, to prevent breakage. A valve chamber B, similar to that previously described,⁵ is sealed to the

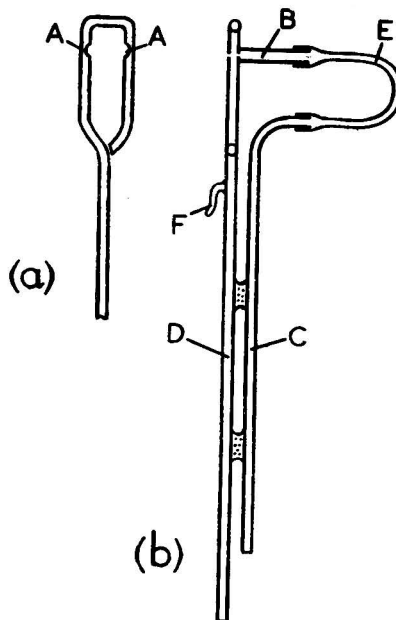


(a)



(b)

Fig. 1



(a)

(b)

Fig. 2

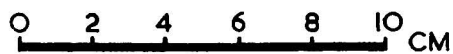
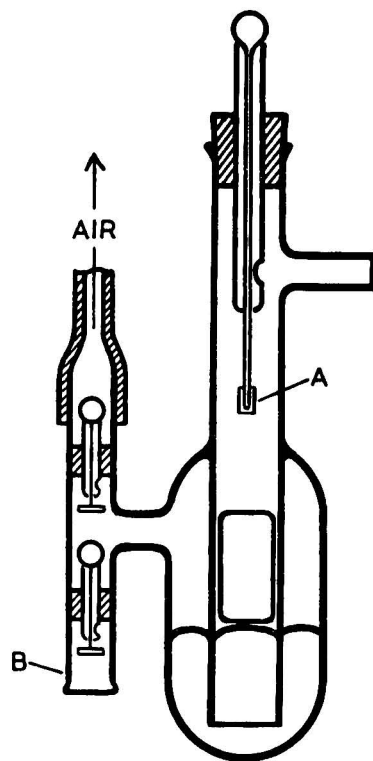


Fig. 3.

outer jacket. Rise and fall of the mercury at about 200 strokes per minute causes air to be drawn in at the lower valve and forced out at the upper one. Insertion of an empty Winchester quart bottle or a 2-litre flask between the pump and the blowpipe gives a steady flame. Suitable adjustment by stopcocks or screwclips gives a hot flame between 3 mm. and 30 mm. in height.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

South African Fish Products. XXVII. Composition of the Liver Oils of the Basking Shark (*Cetorhinus Maximus*, Gunner) and the Spiny Shark (*Echinorhinus Spinosus*, Gmelin). M. L. Karnovsky, W. S. Rapson, H. M. Schwartz and (in part) M. Black and N. J. van Rensburg (*J. Soc. Chem. Ind.*, 1948, **67, 104-107)**—Detailed quantitative study of the saponifiable and unsaponifiable fractions of the liver oils of the basking shark (I) and the spiny shark (II) is described. Results are given for five specimens of I and three of II and for oils from the flesh (tail region), spleen, kidney, epididymia, eye socket, and gristle (underskin) of one basking shark and from the flesh (head region) of another. Unsaponifiable matter of the liver oils of the seven-gilled shark (III) and the souffin shark (IV) was also determined and examined. The hydrocarbons and hydroxylic fractions of the unsaponifiable matter were separated chromatographically by means of activated alumina.

Results—Unsaponifiable matter from I, 30 to 50 per cent., mainly squalene and pristane; from II, about 50 per cent., mainly squalene with some α -glyceryl ethers; from III, about 20 per cent., chiefly α -glyceryl ethers with some sterols; from IV, up to 10 per cent., principally vitamin A, sterols, α -glyceryl ethers, and fatty alcohols. The component fatty acids (weight per cent.) were as shown in the table.

COMPONENT FATTY ACIDS OF THE LIVER OILS OF THE BASKING AND THE SPINY SHARKS, IN WEIGHT PER CENT.

Acids	Basking shark (I)		Spiny shark (II)	
	Saturated	Un-saturated	Saturated	Un-saturated
C ₁₄	2.1	0.5 (-2.0 H)	3.9	1.6 (-2.0 H)
C ₁₆	13.6	11.9 (-2.0 H)	20.4	11.9 (-2.0 H)
C ₁₈	3.2	12.8 (-2.3 H)	6.9	25.6 (-3.0 H)
C ₂₀	3.6	23.2 (-4.0 H)	0.3	15.4 (-6.6 H)
C ₂₂	3.2	20.0 (-3.6 H)	0.2	13.9 (-8.1 H)
C ₂₄	0.4	5.6 (-5.9 H)	—	—

In the relatively low unsaturation of C₂₀ and C₂₂ acids, oil I resembles other shark liver oils rich in squalene, but the average unsaturation of these acids in II is unexpectedly high and the presence of nearly 6 per cent. of C₂₄ acid is also unexpected, as the unsaponifiable matter of II contains much squalene and 13.7 per cent. of α -glyceryl ethers. Oil II therefore does not fit Hilditch's tentative generalisation (Hilditch, "*Chemical Constitution of Natural Fats*," 1941, p. 29). Iodine values given for oils, unsaponifiable matter, and fatty acid indicate that the relationship of high α -glyceryl ether content and lowering of unsaturation of fatty acid also does not hold for basking shark flesh oils.

E. B. DAW

South African Fish Products. XXVIII. Composition of the Liver Oil of the Seven-gilled Shark, *Heptanchias Pectorosus* Garman. M. L. Karnovsky, W. S. Rapson, and H. M. Schwartz (*J. Soc. Chem. Ind.*, 1945, **67, 144-147)**—This liver oil contains a large unsaponifiable fraction, mainly α -glyceryl esters. Characteristics of the oil are: iodine value 118.9, saponification value 159.5, unsaponifiable matter 19.6 per cent., E_{1 cm.}^{1%} of oil at 328 m μ . 1.6. The unsaponifiable matter, examined as previously described (*Idem, Ibid.*, p. 104), had the following percentage composition: α -glyceryl ethers (as selachyl alcohol) 89.2, unsaturated hydrocarbons (as squalene) 1.1, vitamin A 0.5, and cholesterol 6.4, total, 97.2. The α -glyceryl ethers were freed from sterols and acetylated, the acetates fractionated, and the iodine value, saponification value, and "periodic acid equivalent" determined on each fraction. The component α -glyceryl ethers were calculated as in fatty acid calculations—most fractions being calculated as a mixture of C_n and C_{n+2} saturated and mono-ethenoid components. Re-acetylation and fractionation of the "liquid" glyceryl esters indicated the presence of a considerable amount of an unsaturated α -glyceryl ether acetate of side-chain length less than C₁₈; little saturated matter is present. Evidence for C₂₀ and higher fractions is also given. The component fatty acids (weight per cent.) of the saponifiable fraction were:—

	Saturated	Unsaturated
C ₁₄	1.6	0.7 (-2.0 H)
C ₁₆	16.6	11.0 (-2.0 H)
C ₁₈	6.9	30.3 (-2.5 H)
C ₂₀	1.3	15.6 (-5.4 H)
C ₂₂	1.6	13.0 (-8.7 H)
C ₂₄	—	1.4 (-10 H)

The fatty acid composition resembles that of spiny shark oil (*loc. cit.*). The oil does not fit in the tentative generalisation that the presence of large proportions of α -glyceryl ethers in elasmobranch liver oils is associated with marked diminution of polyethenoid unsaturation in C₂₀ and C₂₂ acids. The relative proportions (mol. per cent.) of fatty acids and α -glyceryl ethers containing alkyl residues with the same number of C atoms were compared as follows:—

	α -Glyceryl ethers in α -glyceryl fraction	Fatty acids in fatty acid fraction
C ₁₄ Saturated	—	2.0
C ₁₄ Unsaturated	—	0.9
C ₁₆ Saturated	13.9	18.3
C ₁₆ Unsaturated	19.4	12.3
C ₁₈ Saturated	15.8	6.9
C ₁₈ Unsaturated	41.6	30.5
C ₂₀ Saturated	—	1.2
C ₂₀ Unsaturated	6.2	14.4
C ₂₂ Saturated	—	1.3
C ₂₂ Unsaturated	2.5	11.1
C ₂₄ Saturated	—	—
C ₂₄ Unsaturated	0.6	1.1

Experimental details of the treatment of the bulk sample of unsaponifiable matter, of the determination of saponification equivalent (NaOH being substituted for KOH to prevent periodate precipitation later) and "periodic acid equivalent," and of the separation of "solid" and "liquid" compounds are given. Periodic acid equivalents, determined from consumption of periodic acid after saponification, are not up to standard reproducibility of other determinations on these ethers.

E. B. DAW

Polarimetric Determination of Starch in Cereal Products. K. A. Clendinning (*Canad. J. Res.*, 1948, 26, [F], 185-190)—This paper deals

mainly with the particle-size and the extraction-time requirements in calcium chloride polarimetric procedures for starch in whole wheat and wheat flour. Except for wheat gluten, it is not necessary to grind the samples to an impalpable powder as has often been advocated in the past. Wheat, if ground to pass a 40-mesh screen, is sufficiently fine for the polarimetric determination of starch. Excessive grinding may, in fact, cause low results owing to the increase in solubility. In examining the effects of particle-size on starch recovery, the extraction was carried out as usual (*Idem, ibid.*, 1945, [B], 23, 239-259) for periods of 15, 30, and 45 min. Observations were made in 2-dm. tubes, and protein precipitation and filtration were conducted as usual. As the following table shows, a marked improvement in starch recovery was observed only on the very coarsest sample.

TABLE I

EFFECTS OF PARTICLE-SIZE AND EXTRACTION-TIME ON STARCH RECOVERY FROM WHOLE WHEAT AND GRANULAR FLOURS

Sample	Apparent starch content, * %		
	Ex-tracted 15 min.	Ex-tracted 30 min.	Ex-tracted 45 min.
Whole wheat I:			
2-mm. screen	57.84	60.42	60.42
1-mm. screen	59.09	60.30	60.52
40-mesh	62.09	62.42	62.09
ball-milled	62.32	62.32	62.32
	62.16	61.93	61.60
	62.26	62.04	61.40
	61.66	61.46	61.34
	61.66	61.46	61.46
Whole wheat II:			
1-mm. screen	58.74	58.64	58.17
	58.74	58.74	58.17
40-mesh	59.03	59.03	58.60
	58.93	58.82	58.47
ball-milled	58.81	58.81	58.04
	58.93	58.70	58.04
Granular flour:			
as received	76.82	76.82	76.82
	77.14	76.82	76.82
ball-milled	76.84	76.41	76.18
	76.84	76.61	76.28

TABLE II

COMPOSITION OF WHEAT FLOURS, PER CENT., SOLIDS BASIS

	Whole wheat I	Whole wheat II	Granular flour	Patent flour
Ash	1.92	1.87	0.76	0.48
Fat (by acid hydrolysis)	3.82	4.42	1.45	1.58
Protein	15.09	19.52	13.27	15.04
Total sugar	4.10	4.00	2.34	2.18
Pentosan	6.64	7.25	2.91	1.93
Polyuronide	0.78	0.86	trace	trace
Crude fibre	2.63	2.78	0.71	0.18
Starch by difference	64.82	60.30	78.56	78.61
Polarimetric starch (alcohol extraction)	62.16	59.00	77.25	78.5
Polarimetric starch (stannic chloride precipitation)	62.20	58.96	76.84	78.2

* Data are expressed on a basis of total solids, corrected for ash increments in milling.

With wheat gluten, extraction for 40 min. was necessary, and a particle-size equivalent to 140-mesh was required for maximum results.

Two polarimetric methods (Eva and Rankin) for starch determination were compared with starch obtained "by difference," and the results, with other analytical data, are shown in Table II.

The difference in crude fat obtainable by various extraction methods is shown below.

TABLE III

COMPARISON OF METHODS FOR THE DETERMINATION OF CRUDE FAT IN WHEAT PRODUCTS, PER CENT.

	Ethyl ether*	Light petroleum*	Acid hydrolysis; ether
Wheat starch ..	0.28	nil	0.48
Wheat flour ..	0.71	0.75	1.60
Whole wheat flour	2.08	1.80	3.00
Gluten (100-mesh)	0.63	0.43	5.00

* By 24-hr. Soxhlet extraction.

W. MARTIN

Biochemical

Separation of Tropic and Atropic Acids by Partition Chromatography. S. Gottlieb (*J. Amer. Chem. Soc.*, 1948, **70**, 423)—These acids are separated by partition between chloroform and water adsorbed on silicic acid; an acid-base indicator is incorporated in the aqueous phase.

Procedure—In a mortar, mix intimately 10 ml. of a 0.1 per cent. aqueous solution of 3 : 6-disulpho- β -naphthalene-azo-N-phenyl- α -naphthylamine with 20 g. of dry precipitated silicic acid. Slurry with 50 ml. of chloroform and pour into a 24-mm. diameter glass tube constricted and plugged with cotton wool at the lower end. Allow chloroform to drain until the suspension is stiff, and pipette into the column the solution of tropic and atropic acids (here, 5 mg. of each in 3 ml. of chloroform). When the solution has just passed the top of the column, wash the sides of the tube with 5 ml. of chloroform. Separate and develop the bands with 50 ml. of chloroform. Atropic acid moves rapidly down in a sharp band; wash it through completely. Wash through the upper band of tropic acid with a mixture of 10 per cent. butyl alcohol in chloroform.

G. H. TWIGG

Estimation of Barbituric Acid and Thiobarbituric Acids in Biological Materials. J. Raventos (*Brit. J. Pharmacol.*, 1946, **1**, 210-214)—A method has been developed for estimating barbituric and thiobarbituric acids present together in the same sample. The main feature is the purification of the extracts containing the acids by chromatography; the estimation of barbituric acids is based on Koppanyi's colour reaction (Koppanyi *et al.*, *J. Amer. Pharm. Assoc.*, 1934, **22**, 1076), whilst thiobarbituric acids are determined by Cowan's colour reaction (demonstration to Physiological Society, 1939, and personal communication).

Preparation of activated alumina—Boil 1200 g. of activated alumina (grade O, Messrs. Peter Spence,

Manchester) with 1800 ml. of 10 per cent. acetic acid for 2 hr. Filter and remove the excess of acetic acid by washing with at least 20 litres of hot water. Dry the alumina and heat to 360° C. Cool and add 2.5 per cent. of water to partially deactivate.

Procedure for blood—Mix 10 to 20 ml. volumes of oxalated blood with equal volumes of water and 10 per cent. sodium dihydrogen phosphate solution. Extract with peroxide-free ether in a continuous extraction apparatus at 45° to 50° C. for 8 to 10 hr. Evaporate the ethereal extract to dryness, dissolve the residue in 5 ml. of alcohol-free chloroform, and dry the solution by shaking with 2 g. of anhydrous sodium sulphate. Filter the chloroform solution directly on to an activated alumina column 4 in. high and $\frac{3}{8}$ in. in diameter. Wash the filter three times with 5 ml. of alcohol-free chloroform and pour the washings on to the column. Wash the column with alcohol-free chloroform until the eluate is free from pigment.

Recover the thiobarbituric acids from the column by elution with 50 ml. of 2 per cent. A.R. methanol in chloroform, and then recover the barbituric acids by further elution with 50 ml. of 10 per cent. methanol in chloroform.

Estimation of thiobarbituric acids—Transfer a 2-ml. aliquot of the final chloroform solution to a test tube and add 0.2 ml. of 10 per cent. diethylamine in methanol and 0.5 ml. of a saturated solution of anhydrous copper sulphate in methanol. A green colour develops and is stable for 2 hr. Compare the sample with a series of similarly treated solutions containing 0.03 to 0.5 mg. of the thiobarbituric acid per ml., prepared by dilution of a standard solution containing 0.5 mg. per ml. of the appropriate thiobarbituric acid in chloroform.

Estimation of barbituric acids—For each 2 ml. of the final chloroform solution containing barbituric acids add 0.6 ml. of 5 per cent. isopropylamine in methanol and 0.1 ml. of 1 per cent. cobalt acetate in methanol. Compare the red colour given by the sample with a series of similarly treated solutions containing from 0.1 to 1.0 mg. of the appropriate barbituric acid per ml.

Procedure for urine—Add sufficient concentrated hydrochloric acid to the sample to adjust its reaction to pH 5. Extract with peroxide-free ether in a continuous extraction apparatus at 45° to 50° C. for 8 to 10 hr. Evaporate the ethereal extract to dryness and dissolve the residue in 5 ml. of alcohol-free chloroform. Continue the determination as described for blood.

Procedure for tissues—Grind 10 to 20 g. of tissue sample with sodium dihydrogen phosphate in the proportion of 1 g. of sodium dihydrogen phosphate to every 10 g. of tissue. Add slowly 20 g. of anhydrous sodium sulphate for each 10 g. of tissue and grind the mixture to a fine powder. Transfer the mixture to a desiccator and allow to stand over anhydrous calcium chloride for 1 hr. Extract the powder for 2 to 3 hr. with 50 ml. of A.R. benzene in a flask: filter the extract and wash the flask and residue three times with 15 ml. of benzene. Mix the filtrate and washings and concentrate to 5 ml. by heating at 50° C. under reduced pressure.

Pour the concentrated benzene solution on to an alumina column, wash the flask three times with benzene, and pour the washings through the column. Wash the column with benzene until the eluate is free from pigment and then wash with 20 ml. of chloroform.

Recover and determine the barbituric and thiobarbituric acids by the method described for blood.

Recoveries of barbituric and thiobarbituric acids average 97.3 per cent. A. H. A. ABBOTT

Water Analysis

Water Analyses by Selective Specific Conductance. J. W. Polsky (*Anal. Chem.*, 1947, 19, 657-660)—A simple and rapid method is described for the determination of individual ions in dilute solution, with particular reference to the determination of chloride, sulphate, and calcium in water.

The method involves the measurement of specific conductivity of a sample solution before and after addition of an excess of the appropriate reagent to precipitate the ion being determined. The effect of the reagent addition is to increase the specific conductivity, whilst a decrease is caused by the precipitation taking place. If the amount of reagent added is kept constant, the observed change in specific conductivity can be correlated with the amount of ion being determined.

For the dilute solutions dealt with in water analysis, where the activity of the ions approaches unity, the change in specific conductivity due to addition of a fixed quantity of reagent is virtually independent of the nature of the ions present, provided that the initial specific conductivity of the solutions is the same. For solutions of different initial specific conductivities the change due to the addition of the reagent decreases with increasing initial specific conductivities, owing to lower ionic mobilities at the higher concentrations, and a correction that depends upon the initial specific conductivity must be applied.

The method is of general application providing that the solutions employed are dilute. The procedure for determination of chloride serves to illustrate the technique.

Preparation of standard chloride and conductivity correction curves—Prepare 100-ml. samples of standard sodium chloride solutions to cover the range 0 to 80 p.p.m. of chloride. Pour the first standard into a suitable cylinder, adjust to the desired standard temperature and measure the conductivity with a dipping-type conductivity cell. Transfer the solution to a beaker and, with stirring, pipette in 10 ml. of standard silver nitrate solution (1 ml. \equiv 1 mg. of chloride). Return the solution to the cylinder and again measure the conductivity. Repeat the procedure with the other standards, recording the initial specific conductivity and the change in specific conductivity for each chloride concentration.

To determine the correction to be applied for the initial specific conductivity of the sample, prepare a series of 100-ml. sodium sulphate solutions having a range of specific conductivities of 2 to

700 reciprocal megohms per cm. per cm.² Measure the conductivities as above before and after the addition of 10 ml. of standard silver nitrate solution, recording the change in specific conductivity for each initial specific conductivity. To obtain the conductivity correction for each initial specific conductivity, subtract the change in specific conductivity from the change observed for the solution having an initial specific conductivity of 2 reciprocal megohms. Prepare a graph of conductivity correction against initial specific conductivity.

Apply the conductivity correction to the figure for change in specific conductivity obtained for each chloride standard by adding the conductivity correction corresponding to the initial specific conductivity of the chloride standard. Prepare a graph of the corrected values for change in specific conductivity against chloride concentration.

Determination of chloride—Using 100 ml. of sample, determine the specific conductivity before and after addition of 10 ml. of standard silver nitrate solution. To the observed change in specific conductivity add the conductivity correction corresponding to the initial specific conductivity of the sample and, using this corrected value, read off from the standard chloride curve the chloride concentration of the sample.

Note—The pH of a sample should be observed before starting a determination and, if necessary, addition of acid or alkali should be made to adjust the pH to the range most favourable for precipitation of the ion to be determined. The "initial" specific conductivity is then measured and the determination continued in the normal manner. H. J. CLULEY

Gas Analysis

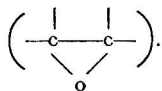
Estimation of Sulphur Trioxide in its Mixtures with Sulphur Dioxide by the Method of Amperometric Titration. D. W. E. Axford and T. M. Sugden (*J. Chem. Soc.*, 1946, 901-903)—An amperometric titration is described for determining sulphur trioxide in the presence of a large excess of sulphur dioxide. The gases are absorbed in sodium hydroxide solution and, after acidification, the sulphur dioxide is blown out by a stream of nitrogen. The sulphate is then titrated with a standard solution of lead nitrate.

Procedure—Pass the gas mixture through 1.0 N sodium hydroxide to absorb the sulphur trioxide and sulphur dioxide. The sodium hydroxide should contain a few drops of glycerol to inhibit the oxidation of sulphur dioxide. Pipette 5 ml. of the solution into a suitable polarographic cell and add 1.0 N nitric acid until the solution is acid to methyl orange. After passing a stream of nitrogen through the solution for 30 min. to drive off the sulphur dioxide, add 1.0 N sodium hydroxide until the solution is just alkaline to methyl orange, followed by 5 ml. of ethyl alcohol to reduce the solubility of the lead sulphate and a small amount of solid lead sulphate to prevent supersaturation. Set the potential of the dropping mercury electrode at -0.8 v. versus the mercury pool and titrate the

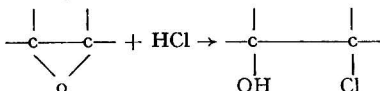
solution with 0.01 *N* lead nitrate, plotting the current flowing against the volume added. The end-point can be read off from the graph with an accuracy of within ± 2 per cent. J. G. WALLER

Organic

Determination of Oxirane Oxygen. D. Swern, T. W. Findley, G. N. Billen, and J. T. Scanlan (*Anal. Chem.*, 1947, 19, 414-415)—Although in the study of atmospheric oxidation of unsaturated fatty materials it is customary to determine the quantity of hydroxyl, carboxyl, carbonyl, and ester oxygen, no work has been reported on the analysis of oxirane oxygen



Nicolet and Poulter (*J. Amer. Chem. Soc.*, 1930, 52, 1186) devised a method for the quantitative opening of the oxirane ring, by means of a solution of anhydrous hydrogen chloride in absolute ethyl ether, for use in the analysis of 9 : 10-epoxystearic acids. The equation



suggests that the method might be specific for oxirane oxygen, and the present authors have examined compounds with and without the group. They conclude that only oxirane oxygen reacts with this reagent; and, by modification of the concentration and the reaction period, the method has been made suitable for use in the analysis of the unknown and complex mixtures encountered in atmospheric oxidation reactions.

Special reagent—Add approximately 25 to 35 ml. of concentrated hydrochloric acid dropwise during about 45 min. to concentrated sulphuric acid. Pass the anhydrous hydrogen chloride into 1500 ml. of absolute ethyl ether until a blank determination indicates that the concentration is 0.19 to 0.20 *N*. To conduct this determination pipette 25 ml. of the solution into 50 ml. of 95 per cent. ethyl alcohol and titrate with 0.1 *N* sodium hydroxide, using a 1 per cent. solution of phenolphthalein in 95 per cent. ethyl alcohol as indicator. Store the reagent in glass-stoppered bottles.

Procedure—Weigh an aliquot of the sample in accordance with the recommendations in Table I, and transfer to a 250-ml. flask fitted with a hollow glass stopper. (Because of its light weight the hollow stopper acts as an automatic safety valve and makes the manual release of pressure unnecessary.) Wash the sides of the flask with 5 ml. of ethyl ether and add 25 ml. of the hydrochloric acid-ether reagent. Stopper the flask, swirl gently to dissolve the sample, and allow to stand for 3 hr. at room temperature. Add 50 ml. of 95 per cent. ethyl alcohol and 1 ml. of a 1 per cent. solution of phenolphthalein in 95 per cent. ethyl alcohol and titrate the excess of acid with 0.1 *N* sodium

hydroxide. Make at least two blank determinations, which must agree within 0.1 ml.

TABLE I

RECOMMENDED SAMPLE WEIGHTS FOR OXIRANE OXYGEN DETERMINATION	
Oxirane oxygen expected, %	Weight of sample, g.
1 to 4	1.0 to 0.8
4 to 8	0.8 to 0.4
8 to 12	0.4 to 0.25
12 to 16	0.25 to 0.20
16 to 20	0.20 to 0.15

Weigh a second sample of from 0.3 to 2.0 g., dissolve it in 75 ml. of freshly neutralised 95 per cent. ethyl alcohol, and titrate to the phenolphthalein end-point with 0.1 *N* sodium hydroxide. For oils insoluble in alcohol, heat the sample under reflux with the alcohol for 5 min., cool to room temperature, and titrate with 0.1 *N* sodium hydroxide.

Calculate the oxirane oxygen from the expression

$$\text{Percentage of oxirane oxygen} = \frac{B - (T - A) \times 1.6}{W}$$

in which *B* = ml. of 0.1 *N* sodium hydroxide used in the blank; *T* = ml. of 0.1 *N* sodium hydroxide used in the back-titration; *A* = acid value of sample expressed as ml. of 0.1 *N* sodium hydroxide used to neutralise the free acid in *W* g. of the sample; *W* = weight of sample in grams.

Table II shows the results obtained when the procedure described above was applied to a selection of purified oxirane compounds. The anomalous result obtained with styrene oxide may be due to the formation of an isomeric aldehyde or ketone by acid catalysis.

TABLE II

Compounds analysed	Per cent. of oxirane oxygen	
	Calcd.	Found
9 : 10-Epoxystearic acid, m.p. 59.5° C.	5.36	5.33
9 : 10-Epoxystearic acid, m.p. 55° C.	5.36	5.35
9 : 10-Epoxyoctadecanol, m.p. 54° C.	5.62	5.65
9 : 10-Epoxyoctadecanol, m.p. 48° C.	5.62	5.60
9 : 10 : 12 : 13-Diepoxystearic acid, m.p. 78° C.	10.2	9.16
Methyl 9 : 10-epoxystearate, m.p. 16° C.	5.12	5.08
Methyl 10 : 11-epoxyhendecanoate	7.47	7.28
Epichlorohydrin	17.3	16.8
Glycidol	12.6	12.3
1 : 2-Epoxyoctane	12.5	12.0
1 : 2-Epoxydecane	10.2	10.0
1 : 2-Epoxydodecane	8.68	8.53
1 : 2-Epoxytetradecane	7.54	7.53
1-Phenyl-1 : 2-epoxyethane (styrene oxide)	13.3	11.7

A. H. A. ABBOTT

Determination of Sulphur in Bone Char. V. R. Deitz, H. R. Higginson, and C. Parker (*J. Res. Nat. Bur. Stand.*, 1948, 40, 263-274)—The determination of sulphate sulphur by treatment of bone char with hydrochloric acid, and of total sulphur by treatment with nitric acid, using established procedures, gives inaccurate results owing to the presence of organic sulphur. The barium sulphate precipitate can be freed from calcium and from phosphate by dissolution in 70 per cent. perchloric acid and re-precipitation.

Method 1—Total sulphur—Treat 5 g. of bone char, dried at 105° to 110° C. for at least 4 hr., in a 800-ml. beaker with 10 to 15 ml. of water and 25 ml. of concentrated nitric acid. Boil gently for 1.5 hr., add 15 ml. of 70 per cent. perchloric acid (stage B) and heat until the char is completely oxidised. Cool, dilute with 100 ml. of water, and filter through a No. 40 Whatman paper (stage A) into a 1500-ml. beaker. Wash the residue with 150 to 200 ml. of water, dilute to 750 to 800 ml. and adjust the pH to 1 (glass electrode) with aqueous ammonia. Heat to 50° C., add 50 ml. of 5 per cent. barium chloride solution dropwise with mechanical stirring, keep at 50° C. for 4 hr., and filter through a No. 42 paper. Wash until only a trace of chloride is detectable. Transfer paper and precipitate to a 800-ml. beaker, add 25 ml. of nitric acid, warm to destroy the paper, add 15 ml. of perchloric acid, and continue boiling for 15 min. after the nitric fumes have ceased, to give a colourless or slightly yellow solution. Cool to room temperature, add 400 ml. of water and 5 ml. of 5 per cent. barium chloride solution, and adjust the pH to 1. Leave to stand overnight, filter, wash, ignite, and weigh.

Method 2—Sulphur in the filtrate from acid leaching—Add slowly 100 millilitres of diluted hydrochloric acid (1 + 1) to 10 grams of the bone char wetted with 25 ml. of water in a 800-ml. beaker. Heat under a cover for 1.5 hr. at 80° to 90° C. Cool, dilute accurately in a 250-ml. calibrated flask, and filter exactly 200 ml. through a No. 40 paper into a 200-ml. calibrated flask. Determine the inorganic sulphate in this filtrate as in Method 1, starting at stage A. Multiply the result by $(250 - w/1.8)/200$, where w is the dry weight in grams and 1.8 is the density of the carbonaceous residue.

Method 3—Combined organic sulphur—To the remaining filtrate in the 250-ml. flask, the residue, and the filter paper obtained in Method 2, add 25 ml. of nitric acid and heat until the paper is decomposed. Add 15 ml. of perchloric acid and determine the sulphate as in Method 1 from stage B. Subtract from the result the sulphur figure, obtained by Method 2, multiplied by $(50 - w/1.8)/(250 - w/1.8)$.

Method 4—Sulphide sulphur—Connect to an Erlenmeyer flask with a ground-glass joint a low-pressure air supply, a dropping funnel and, through a reflux condenser, two fritted-disc gas-washing bottles in series. Place in the gas-washing bottles a solution obtained by diluting to 100 ml. one millilitre of a solution containing 168 g. of cadmium sulphate, 960 ml. of concentrated aqueous ammonia, and 1046 ml. of water. Cool the first bottle in ice.

Place 5 g. of the bone char in the flask and run in slowly 50 ml. of diluted hydrochloric acid (1 + 1). After the first reaction sweep out with air and heat gently for 20 min. Add 25 ml. of concentrated hydrochloric acid to the wash bottle solution and titrate with iodine, using starch as indicator. Subtract the value given by a blank determination.

C. F. HERBERT

Identification of Organic Acids and Nitrophenols by their Benzylammonium salts. R. Boudet (*Bull. Soc. Chim.*, 1948, 390-392M)—The methods of preparation are designed to avoid contamination of the salts with the carbonate of the base. Drying by long exposure in the air is avoided because the salts are somewhat hygroscopic. The failure of Buchler *et al.* (*J. Amer. Chem. Soc.*, 1935, 57, 2181) to observe these precautions is the probable reason for numerous discrepancies between the m.p. given by them and those now determined. The neutral salts of polybasic acids are more readily purified than the acid salts and the former are therefore prepared.

Procedure for monobasic acids and nitrophenols—Take 1 to 3 g. of the acid according to the molecular weight. If the molecular weight is unknown, take 3 g. to ensure an excess. Dissolve this sample in benzene, with addition of a small amount of alcohol if necessary, and add 2 ml. of a water-free mixture of equal volumes of benzylamine and benzene. Agitate the mixture vigorously and allow to cool and crystallise. If it is not possible to induce crystallisation by ordinary means, the solution can be diluted with light petroleum, but there is then a risk of precipitating the excess of acid. Alternatively, the salt can be extracted with water, the aqueous solution washed with ether to remove free acid, and the derivative obtained by evaporation to dryness on a water-bath. Wash the filtered salt with a solvent that dissolves the free acid selectively, such as benzene or benzene-alcohol or benzene-light petroleum mixtures. Recrystallise from carbon tetrachloride mixed, if necessary, with the minimum quantity of alcohol, filter at the pump, leave on the pump for about 15 min. and determine the melting-point.

Procedure for polybasic acids—Dissolve 0.2 to 0.3 g. of the acid in the minimum quantity of alcohol, add 1 ml. of benzylamine, and shake. After a few minutes, redissolve the precipitated salt by boiling, adding a little more alcohol if necessary. On cooling, the salt crystallises, any carbonate formed remaining in solution. Filter at the pump, wash with a little alcohol, leave on the pump for about 15 min., and determine the m.p.

The following are the m.p. (in ° C.) of the salts of the acids named: *n*-butyric, 54-55*; *n*-valeric, 56-57; propionic, 68; lauric, 70-73.5*; stearic, 70.3-70.5; caproic, 71.5-72; oenanthic, 73.2-73.8; isovaleric, 74-76*; cyclopropane-carboxylic, 74.5-75; caprylic, 75-76; myristic, 77-78; palmitic, 79-79.5; isobutyric, 92-93; 4-chlorocrotonic (*trans*), 93.5-94.5; acetic, 97.5-98.5; 2-hydroxy-3:4-dibromobutyric, 100-101*; formic, 100-101; *p*-nitrophenol,

* Bad m.p.

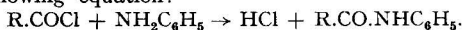
103-103.5; dichloroacetic, 105-105.5; trichloroacetic, 118-119 (decomp.); anthranilic, 113-114; 2-chlorocrotonic (*trans*), 114-115; chloroacetic, 120-121.2; *o*-nitrophenol, 121-121.5; sebacic, 121.5-122.5; phenylacetic, 122-123; citraconic, 125-125.5; malic, 126.5-127; benzoic, 129-129.5; cyanoacetic, 131-131.5 (decomp.); itaconic, 132-133; cinnamic, 131-131.5; malonic, 142.5-143; anisic, 143.5-144.5; *o*-nitrobenzoic, 147-148.5; succinic, 147.5-148; 2 : 5-dinitrophenol, 147.5-148; tartaric, 147.5-148; 2-ethoxymalonic, 155-155.5 (decomp.); 1-cyanocyclopropane-1-carboxylic, 156.5-157.5; adipic, 162.5-163.5; *p*-toluic, 164-164.5; 2 : 6-dinitrophenol, 166-167; tartaric, 170-172; fumaric, 171-172; 2 : 4-dinitrophenol, 171.3-171.5; cyclopropane-1 : 1-dicarboxylic, 173-173.5 (decomp.); *m*-nitrobenzoic, 177-178; camphoric, 179-181; fumaric, 181-182; phthalic, 184.5-185; gallic, 188-190; trinitrophenol, 195-196; oxalic, 195-196; *p*-nitrobenzoic, 198-199; 2-chloro-3 : 4-dibromobutyric, 200-205.*

The salt of mucic acid, m.p. 200° C., is prepared by mixing an excess of the acid with benzylamine and extracting the mixture with cold dilute alcohol.

It is generally possible to prepare the benzylamide by heating the benzylammonium salt for 1 hr. in the air. The m.p. of the benzylamide can then be determined as a confirmatory test (Dermer and King, *J. Org. Chem.*, 1943, 8, 168).

W. C. JOHNSON

Titration of Acyl Chlorides. M. Pesez and R. Willemart (*Bull. Soc. Chim.*, 1948, 479-480M)—The method uses the reaction represented by the following equation:



Any free organic acid present does not enter into this reaction and is subsequently titrated, together with the hydrochloric acid liberated. Further titrations of the total acid and of the chloride, after hydrolysis, provide the necessary data for calculating the constitution of the sample. Dioxan is used as the solvent by reason of its miscibility with water, its good solvent properties for organic acids and acid chlorides, and the ease with which it is obtained free from water and alcohol by rectification over sodium.

Procedure—(1)—Dissolve a quantity, *p* g., of the sample, equivalent to 10 to 15 ml. of 0.1 *N* silver nitrate, in 15 ml. of dioxan, add 10 ml. of water, and titrate with 0.1 *N* sodium hydroxide to the green colour of bromothymol blue. Volume of 0.1 *N* sodium hydroxide required = *a* ml. (2)—To the same solution add 5 ml. of diluted nitric acid (1 in 5), 20 ml. of 0.1 *N* silver nitrate, and 10 drops of a saturated, aqueous solution of potassium permanganate. Decolorise by adding a few drops of 3 per cent. hydrogen peroxide, free from halogens, and titrate with 0.1 *N* potassium thiocyanate, using ferric alum as indicator. Volume of 0.1 *N* silver nitrate equivalent to chloride present = *c* ml. (3)—Dissolve a further quantity, *p'* g., of the acid chloride in 10 ml. of dioxan and add 2 ml. of freshly distilled aniline. Stir for a few seconds, add 100 ml. of water, and titrate with 0.1 *N* sodium hydroxide,

using bromothymol blue as indicator. Volume of 0.1 *N* sodium hydroxide required = *b* ml.

If *M* = molecular weight of the acid chloride and *m* = that of the organic acid, then:

Acid chloride, per cent. =

$$\left(\frac{a}{p} - \frac{b}{p'}\right) \times \frac{100 M}{10,000}$$

Organic acid, per cent. =

$$\left(\frac{b}{p'} - \frac{c}{p}\right) \times \frac{100 m}{10,000}$$

Free hydrochloric acid, per cent. =

$$\left(\frac{c-a}{p} + \frac{b}{p'}\right) \times \frac{36.5 \times 100}{10,000}$$

The method is applied to the analysis of acetyl chloride, benzoyl chloride, and its *p*-nitro- and 3 : 5-dinitro- derivatives, and to the chloride of acetylsalicylic acid.

W. C. JOHNSON

(A) Aldehydes and the Doebner-Miller Reaction. (1) 5-Carboxy-7-aminoquinaldine. (2) Detection of the $-CH_2CHO$ Group. L. Velluz, G. Amiard, and M. Pesez. (3) Estimation of Acetaldehyde. L. Velluz, M. Pesez, and M. Herbain. (B) A New Fluorescence Indicator. L. Velluz and M. Pesez (*Bull. Soc. Chim.*, 1948, 678-679M, 680-681M, 681-682M, 682-683M)—(A) (1)—von Bitto (*Z. anal. Chem.*, 1897, 36, 369) found that strongly fluorescent substances are produced by the reaction of *m*-phenylenediamine salts with aldehydes, but he isolated no definite compounds. The analogous product from the condensation of 3 : 5-diaminobenzoic acid with acetaldehyde is now prepared, and is shown to be 5-carboxy-7-aminoquinaldine. This substance also exhibits a green fluorescence in acid solutions.

Preparation of 5-carboxy-7-aminoquinaldine—To an ice-cold mixture of 10 ml. of paraldehyde and 10 ml. of ethyl alcohol slowly add 50 ml. of a 50 per cent. aqueous solution of 3 : 5-diaminobenzoic acid dihydrochloride previously cooled to 0° C. After keeping for several hours at 15° to 17° C., filter off the yellow needles of 5-carboxy-7-aminoquinaldine hydrochloride and wash them with water. The water decomposes the hydrochloride; 4 g. of the amino acid are obtained. Dissolve the product in 5 volumes of 1.0 *N* sodium hydroxide, add charcoal, filter, and reprecipitate with carbon dioxide. Filter off, wash with water, and dry at 100° C. The product contains 1 mol. of water of crystallisation. Alternatively, the crude product may be purified by recrystallisation from 60 volumes of boiling acetic acid followed by the above process of reprecipitation to obtain the hydrate.

(2) The reaction already described does not occur with the common ketones and is confined to aldehydes that contain an α -methylene group. It may be used as a sensitive test for acetaldehyde and thus, indirectly, for a number of other substances such as ethyl alcohol and lactic acid.

Procedure—Dissolve 2 g. of 3 : 5-diaminobenzoic acid hydrochloride in 50 ml. of phosphoric acid

* Bad m.p.

(density 1.62) and dilute to 100 ml. with water. Decolorise, if necessary, with charcoal. Add to the aldehyde solution an equal volume of the above reagent. A yellow colour and a yellow-green fluorescence develop more or less rapidly according to the concentration of aldehyde. For concentrations of acetaldehyde of the order of 10^{-4} the fluorescence is directly perceptible after 15 min. heating on a water-bath. Concentrations down to 2×10^{-6} may be detected, after several hours standing, by the use of an ultra-violet lamp.

m-Phenylenediamine hydrochloride can be used in place of the diaminobenzoic acid hydrochloride. The sensitivity for acetaldehyde is then 3×10^{-5} after 1 hr. and 2×10^{-5} after 24 hr.

(3) The intensity of the fluorescence of 5-carboxy-7-aminoquinoline varies with the acidity of the solution, becoming less intense in solutions of low pH. By the use of phosphoric acid these variations are minimised and the fluorescence intensity is a linear function of the acetaldehyde concentration between 10^{-4} and 10^{-6} .

Reagent—Prepare an aqueous solution containing 10 g. of 3 : 5-diaminobenzoic acid dihydrochloride in 100 ml. and filter through "Acticarbhone," if necessary, to remove any fluorescent impurities.

Standard—Dissolve 50 mg. of 5-carboxy-7-aminoquinoline in 1 litre of a 5 per cent. solution of hydrochloric acid. To 2 ml. of this solution add 10 ml. of 7 M phosphoric acid and dilute with water to 100 ml. The parent solution is stable in the dark, but the diluted standard (1 ml. = 1 μ g. of carboxy-aminoquinoline) should be renewed after each determination.

Fluorimetric procedure—To 3 ml. of a solution containing 10 to 100 μ g. of acetaldehyde add 2 ml. of the reagent and 5 ml. of 7 M phosphoric acid, heat over boiling water for 10 min. and leave in a water-bath at 15° to 17° C. for 2 hr. Add 5 ml. of 7 M phosphoric acid and dilute with water to 20 ml. Determine the fluorescence intensity with reference to that of the standard, using the Meunier electrophotometer with a green filter.

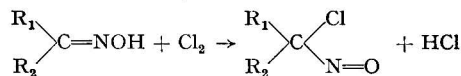
(B) The fluorescence of an acid solution of 5-carboxy-7-aminoquinoline disappears when such a solution is made alkaline, but the change is not well marked with respect to any definite pH value. The N-acetyl derivative of the same substance shows a bright violet-blue fluorescence, which fades sharply over the narrow range pH 7.6 to 8. The acetyl compound may, therefore, be employed as a fluorescence indicator in the titration of weak acids.

Preparation of 5-carboxy-7-acetylaminoquinoline—Heat under a reflux condenser for 1 hr. a suspension of 5-carboxy-7-aminoquinoline in 10 ml. of acetic anhydride. Cool, add 50 ml. of water, allow to react, and partly neutralise with sodium hydroxide. Recrystallise the precipitated acetyl derivative from 250 ml. of boiling water, decolorising with charcoal. M.p. 315° C. (decomp.).

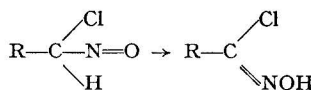
Prepare a solution of 0.1 g. in 1 litre of 50 per cent. ethyl alcohol and use 0.1 ml. of this solution in acidimetric titrations. For coloured solutions, 1 ml. of a 0.05 per cent. solution is recommended.

W. C. JOHNSON

Detection and Colorimetric Estimation of Oximes, Ketones, and Hydroxylamine. O. Wichterle and M. Hudlicky (Coll. Czech. Chem. Comm., 1947, 12, 661-670)—Chlorine and other chlorinating agents convert oximes into intensely blue chloronitroso compounds (Piloty and Stock, *Ber.*, 1902, 35, 3093).



Those derived from aldoximes rapidly rearrange to colourless hydroxamic acid chlorides,



but the ketoximes yield chloronitroso derivatives sufficiently stable for colorimetric estimation. The reaction can be employed qualitatively and quantitatively for ketones that readily form oximes, and for hydroxylamine. *Cyclohexanone* oxime, for example, is detectable at a dilution of 1 : 10,000 in 10 ml.

Preparation of chlorinating agent—Moisten 60 g. of urea with 15 ml. of water, cool below 0° C., and pass in chlorine until the weight has increased by 30 to 32 g. Remove the crystals. The syrupy liquid decomposes slowly, but is usable for several weeks as it is employed in considerable excess.

Detection of oximes—To a solution of the substance in an organic solvent add several drops of the chlorinating agent. The presence of an oxime is shown by a blue colour. If the sample is dissolved in water the blue substance may precipitate and extraction with an organic solvent is then desirable.

Detection of ketones—Add an excess of a solution containing 8.2 g. of hydroxylamine sulphate and 13.7 g. of crystalline sodium acetate in 1 litre of water and proceed as in the previous paragraph.

Detection of hydroxylamine—Neutralise any mineral acid with sodium acetate, add *cyclopentanone* and a few drops of chlorinating agent and shake with xylene.

The same principles are applied to the colorimetric estimation of *cyclohexanone* oxime, *cyclopentanone* oxime, *cyclohexanone*, and hydroxylamine. The most suitable solvent is glacial acetic acid. If the reaction is carried out in dilute acetic acid the results are not reproducible, but once the colour is formed in the concentrated acid, dilution has no effect, except to precipitate the chloronitroso compound if carried to excess. The extinction of a 0.01 M solution of chloronitrosocyclohexane decreases by 2 per cent. per hour, but this does not affect significantly determinations carried out with normal dispatch. The extinction curves for 1-chloro-1-nitrosocyclohexane and 1-chloro-1-nitrosocyclopentane, determined in acetic acid solution with a Lange universal colorimeter and a Soudan 5B filter, employing the deviation method, are linear for concentrations up to 0.01 M. These characteristics are determined on samples of the pure chloronitroso compounds, the preparation of which is described. When using the method for the control of the manufacture of ϵ -caprolactam

from cyclohexanone oxime the presence of the lactam leads to slightly high results, and the presence of sulphuric acid to low results. Sulphuric acid must therefore be neutralised with a solution of fused sodium acetate in glacial acetic acid.

Estimation of cyclohexanone oxime—Dissolve the sample containing 0.01 to 0.06 g. of the oxime in 10 ml. of acetic acid and add 0.2 to 0.3 ml. of an aqueous solution of chlorinated urea. Add 30 ml. of water and dilute to 50 ml. with acetic acid. Measure the extinction of the solution and read the concentration from a calibration graph. The graph should be checked frequently. The error is ± 2 per cent. for 0.005 to 0.01 M solutions, but for less than 5 mg. per 50 ml. the error may be 30 per cent.

Estimation of cyclopentanone oxime—Dissolve the sample containing 0.01 to 0.05 g. of the oxime in 10 ml. of acetic acid, add 0.25 ml. of chlorinating agent and 25 ml. of water, and dilute to 50 ml. with acetic acid. The solutions used for calibration must also contain 50 per cent. of acetic acid since the acid concentration affects the colour intensity of chloronitrosopentane solutions.

Estimation of cyclohexanone—To the sample containing 0.01 to 0.05 g. of the ketone add 3 ml. of 0.5 M hydroxylamine acetate. After 5 to 10 min., add 20 ml. of acetic acid and 0.5 ml. of chlorinating agent, and dilute to 50 ml. with water. The calibration curve prepared for the oxime serves also for the ketone.

Estimation of hydroxylamine—Dissolve the sample containing the equivalent of 0.01 to 0.035 g. of the hydrochloride in 1 ml. of 0.2 M sodium acetate, add 0.1 ml. of cyclohexanone, 20 ml. of acetic acid, and 0.25 ml. of chlorinating agent, and dilute to 50 ml. with water. Alternatively, the estimation may be carried out in aqueous solution if a keto acid is used in place of cyclohexanone. Dissolve the sample containing 0.01 to 0.04 g. of the hydroxylamine salt in 5 ml. of water and add 3 N sodium hydroxide to the colour change of phenolphthalein; add 2 ml. of a 0.5 M solution of cyclohexanone-3 : 4-dicarboxylic acid and, after 2 to 5 min., 0.5 to 1 ml. of chlorinating agent, and dilute to 50 ml. with water. The calibration curve is constructed with the use of reagent hydroxylamine hydrochloride.

W. C. JOHNSON

Analysis of Aliphatic Amine Mixtures. Determination of Tertiary Amines in the Presence of Primary and Secondary Amines and Ammonia. C. D. Wagner, R. H. Brown, and E. D. Peters (*J. Amer. Chem. Soc.*, 1947, 69, 2609-2610)—The method of Blumrich and Bandel (*Angew. Chem.*, 1941, 54, 374) consists of treatment with acetic anhydride and titration of the unacetylated tertiary amine with perchloric acid in acetic acid. The method is now shown to be capable of general application except to mixtures containing secondary amines in which the nitrogen is attached to secondary alkyl groups. More vigorous conditions are prescribed for such sterically-hindered substances. When these conditions are adopted the presence of some acetic acid is necessary to prevent significant decomposition of the tertiary amine.

Reagent and apparatus—Prepare 0.1 N perchloric

acid by mixing the appropriate amount of the 70 per cent. acid with glacial acetic acid, and standardise against anhydrous sodium carbonate dissolved in acetic acid, titrating potentiometrically or to the crystal-violet end-point. For the potentiometric methods the authors used glass and calomel electrodes with a direct reading Beckman Model M or Precision-Shell (Penther and Rolfson, *Ind. Eng. Chem., Anal. Ed.*, 1943, 15, 337) titrometer. In the examples quoted the end-point inflections in the titration curves are in the region of 300 to 400 millivolts electrode potential.

General procedure—Add not more than 2 g. of the sample, containing not more than 1 g. of water, to 20 ml. of acetic anhydride containing 2 ml. of acetic acid, and allow the mixture to stand for 3 hr. at room temperature. Then add 30 ml. of acetic acid and titrate the mixture potentiometrically with 0.1 N perchloric acid in acetic acid.

Special procedure for sterically-hindered secondary amines—The method is similar to the general procedure except that the mixture is "gently refluxed" for 1 hr. instead of being kept at room temperature for 3 hr.

In presence of large amounts of amides the end-point is often slightly buffered, but when the sample consists of essentially pure tertiary amine the end-point is sharp and crystal violet can be used as a colorimetric indicator in place of the potentiometric procedure. The use of the indicator in the analysis of any particular mixture, however, should first be investigated by parallel experiments using the indicator and the potentiometric method on a typical sample.

W. C. JOHNSON

Analysis of Aliphatic Amine Mixtures: Determination of Secondary plus Tertiary Amines by the Azomethine-Acidimetric Method. C. D. Wagner, R. H. Brown, and E. D. Peters (*J. Amer. Chem. Soc.*, 1947, 69, 2611-2614)—If an aromatic aldehyde is added to a mixture of a primary and a secondary amine and the mixture titrated potentiometrically in a non-aqueous solvent, a sharp end-point corresponding to the neutralisation of the secondary amine is observed. The azomethine, formed by reaction of the primary amine with the aldehyde, is a much weaker base and gives rise to a less distinct end-point. The primary amine may be assayed by this second end-point but is better determined by difference after titration of the total bases. Ammonia, in absence of water, titrates as primary amine but, when water is present, interferes with the secondary amine end-point and must be separated. In the procedure recommended (*infra*) quantities of ammonia down to 0.37 mg.-equivalents cause significant error when 5 g. of water are also present. A method for the separation and determination of ammonia is described. When ammonia is absent the sample of amines may contain as much as 95 per cent. of water. Tertiary amines, when present, do not react with the aldehyde and are determined with the secondary amines. They may be determined separately by the method described in the preceding abstract.

Reagents—(1) Hydrochloric acid, 0.5 N, in isopropyl alcohol. Mix one volume of concentrated

hydrochloric acid with isopropyl alcohol to give a total of 24 volumes and standardise against a standard alkali. (2) Salicylaldehyde free from salicylic acid. (3) Sodium cobaltinitrite solution. Dissolve 25 g. of pure cobalt nitrite and 25 g. of sodium nitrite in water and dilute to 200 ml.

Apparatus—The authors recommend the Beckman Model M or the Precision Shell (Penther and Rolfsen, *Ind. Eng. Chem., Anal. Ed.*, 1943, 15, 337) direct-reading titrometer with glass and calomel electrodes and a 10-ml. burette, reading to 0.05 ml.

Procedure—Add the sample, containing about 4 mg.-equivalents of secondary amine, to 80 ml. of methanol and 5 ml. of salicylaldehyde. Mix, cover with a watch-glass, and allow to stand for 30 min. Titrate potentiometrically with 0.5 N hydrochloric acid in isopropyl alcohol. Calculate the secondary (plus tertiary) amine as equivalent to the acid used in titrating to the first end-point. Determine the total bases by a separate titration and calculate the primary amine by difference.

Separation and determination of ammonia—Neutralise the sample, which may contain 15 to 20 mg.-equivalents of amine, in an ice-bath with hydrochloric acid, dilute to about 25 ml. with water, and add 25 ml. of sodium cobaltinitrite solution. Allow to stand for 1.5 hr. in the ice-bath, add 40 ml. of Methyl Cellosolve, and leave in the ice-bath for 30 min. more. Use suction to filter off the precipitate of sodium diammonium cobaltinitrite on an asbestos filter, wash with 50 ml. of 50 per cent. Methyl Cellosolve, and transfer the precipitate, with the asbestos, to a distilling flask. Add an excess of sodium hydroxide solution, distil the liberated ammonia into boric acid solution, and titrate in the usual manner. If the presence of both ammonia and water has prevented titration of secondary amines in the original sample, they may now be determined by the general procedure, after recovery from the filtrate from the cobaltinitrite precipitate by the following method. Transfer the filtrate, immediately after filtration, to a distilling flask, add an excess of sodium hydroxide solution, distil 50 ml. into 45 ml. of cold methanol, dilute to 100 ml., and take a 10- to 15-ml. aliquot for the azomethine method.

Results on 17 known mixtures of amines (not including ammonia) show errors varying between - 1.6 and + 1.3 per cent. of the quantity of secondary amine present. Allylamines, methallylamines, ethanolamines, diethylenetriamine, dimethylamine plus butylamine, and piperidine plus ethylamine give end-points that are satisfactory, but less sharp than others. Diethanolamine reacts with salicylaldehyde, probably forming an oxazolidine, but this compound hydrolyses during the titration if 5 ml. of water are added. The secondary amino group of diethylenetriamine is only weakly basic, but its basicity is greatly increased by the addition of salicylaldehyde. The probable reason for this is discussed.

The use of benzaldehyde for azomethine formation leads to unsatisfactory results for a number of secondary amines. A reason for this is suggested and several reasons for the adoption of salicylaldehyde are stated.

The ammonia separation is not applicable in presence of methylamine since the latter yields a cobaltinitrite that is only slightly soluble. Recovery of higher-boiling amines is not complete by the prescribed procedure; a loss of about 5.6 per cent. is shown for *n*-butylamine. W. C. JOHNSON

Determination of Halogens in Organic Substances by Hydrogenation. M. Pesez and P. Poirier (*Bull. Soc. Chim.*, 1948, 379-381M)

—In the Raney nickel reduction method of Schwenck *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1943, 15, 576) the alloy must be added very slowly, at 0° C., to avoid the excessively vigorous evolution of hydrogen. The authors' method provides a simple means of avoiding this difficulty, but it is not applicable to certain volatile compounds such as chloro- and bromo-benzenes in which the halogen is not sufficiently mobile.

Procedure—In a test tube dissolve a quantity of the substance equivalent to 10 to 15 ml. of 0.1 N or 0.02 N silver nitrate, in 10 ml. of methanol. Add 10 ml. of 20 per cent. sodium hydroxide solution, 2 g. of zinc powder, and 0.5 g. of coarsely powdered Raney alloy containing 33 per cent. of nickel. Fit a reflux condenser and heat over boiling water, maintaining a constant evolution of hydrogen for 1 hr. Allow to cool, decant the liquid, wash the residue of zinc by decantation with two 20-ml. portions of water. Add 10 ml. of nitric acid to the mixed liquid and washings and complete the determination by the Volhard titration.

The effect of the Raney nickel is apparently catalytic since the reduction is incomplete in its absence. The following compounds yield satisfactory results: *p*-chloro-*m*-cresol, *p*-chloronitrobenzene, tribromophenol, bromocamphor, bromotriphenylethylene, bromosuccinimide, eosin, 1-(2'-bromoethyl)-6-methoxynaphthalene, dibromotyrosine, 2:4-dibromoandrosterone, di-iodotyrosine, and di-iodothymol. W. C. JOHNSON

Determination of Glycerophosphoric Acid. Application to Phosphatides. T. Cahn, J. Houget, and R. Agid (*Bull. Soc. Chim.*, 1948, 666-668M)

—The addition of barium acetate solution to a dilute aqueous solution of sodium glycerophosphate produces no precipitate, but the further addition of 5 volumes of methyl alcohol precipitates the barium salt almost quantitatively. The precipitate is less soluble on heating. After boiling, filtering, washing with 83 per cent. methyl alcohol, and drying over sulphuric acid in a vacuum desiccator the material weighs 110 to 130 per cent. of the theoretical value. After reprecipitation with methyl alcohol from an acetate solution the substance is not pure barium glycerophosphate; it contains only about 9.2 per cent. of phosphorus (theory = 9.82 per cent.), but entrainment of the solutes compensates for losses due to solubility, and the results are correct to within 2 per cent. when calculated according to the theoretical factor 1 g. of barium glycerophosphate = 0.542 g. of glycerophosphoric acid. The experiments were carried out with pure specimens of sodium α - and β -glycerophosphate.

Procedure—Dissolve in 7 ml. of water a quantity of sodium glycerophosphate equivalent to 0.05 to 0.20 g. of glycerophosphoric acid. Add 0.7 ml. of a 50 per cent. solution of barium acetate (equivalent to 0.217 g. of glycerophosphoric acid) and 40 ml. of methyl alcohol, boil for a moment on a water-bath, and allow to stand 2 hr. Centrifuge, using 5 ml. and 3 ml. of 83 per cent. methyl alcohol to wash the precipitate into the tube. Dry the precipitate and dissolve it in the centrifuge tube, using 4 ml. and three 1-ml. quantities of 0.01 *N* acetic acid containing 0.1 *M* sodium acetate, centrifuging after each treatment so as to decant only clear liquid. Add to the solution 0.36 ml. of 0.25 *N* barium hydroxide (the *pH* should now be about 9.3) and, immediately, 40 ml. of methyl alcohol. Complete as after the initial precipitation, and weigh.

Determination of glycerophosphoric acid in phosphatides—Saponify the material by boiling with 1.0 *N* alcoholic potassium hydroxide for 2 hr. Add water and sulphuric acid until the mixture is 50 per cent. with respect to alcohol and 0.1 *N* with respect to alkali, and extract the unsaponifiable matter with light petroleum. Make acid with sulphuric acid and extract the fatty acids. Make just alkaline to phenolphthalein with potassium hydroxide and evaporate to dryness on a water-bath. Redissolve in 5 ml. of water, add 50 ml. of methyl alcohol, filter, and wash the residue of potassium sulphate with 90 per cent. methyl alcohol. Evaporate the alcoholic solution to dryness and redissolve in 7 ml. of water. From this point follow the process of precipitation with barium acetate described above. The barium salt obtained contains only 5.7 to 8.5 per cent. of phosphorus, varying with the nature of the phosphatide. It is impossible, therefore, to complete the analysis simply by weighing the precipitate. Dissolve the first precipitate in 7 ml. of acetic acid-acetate solution and determine the total phosphorus and the inorganic phosphorus, and thence the glycerophosphate phosphorus by difference.

The precision claimed is to within 3 to 4 per cent. Boiling with 1.0 *N* alcoholic potassium hydroxide for 2 or 7.5 hr. causes no appreciable hydrolysis of glycerophosphoric acid.

W. C. JOHNSON

Chromatographic Analysis of Synthetic Mixtures of Isomeric Trimethylglucoses. R. A. Boissonnas (*Helv. Chim. Acta*, 1947, 30, 1689-1703)—The methylglucoses are hydrogenated and converted into the corresponding *p*-phenylazobenzoyl ("azoyl") glucitols, which are separated chromatographically on alumina. Azoyl methylglucitols corresponding to the following sugars were separated from binary mixtures: 2 : 3 : 4 : 6-tetramethylglucose, 2 : 3 : 4-, 2 : 3 : 6-, 2 : 4 : 6- and 3 : 4 : 6-trimethylglucose, and 2 : 3-dimethylglucose.

Procedure—Neutralise alumina (Merck) by stirring for 3 hr. on a water-bath with 3 *M* nitric acid and washing to neutrality with hot water. Dry at 120° C. for 6 hr. and heat to dull red-heat for 1 hr. To obtain alumina of activity I (characterised by the method of Brockmann and Schodder, *Ber.*,

1941, 74, 73) add 5 per cent. by weight of distilled water to the calcined alumina, shake for 10 hr., and dry at 120° C. for 6 hr. For alumina of activity III add 3 per cent. by weight of distilled water to alumina I and shake for 10 hr. Spent alumina is recoverable by washing with boiling methanol containing 2 per cent. of water, and re-processing as above.

Use 1 ml. of alumina per mg. of substance to be treated chromatographically, and make the height of the alumina column seven times its diameter. To separate the tetramethyl from the trimethyl compounds, use benzene as solvent and developer, and alumina III as adsorbent. To separate the trimethyl compounds from each other and from the dimethyl compound, use chloroform as solvent and developer, and alumina I as adsorbent.

At the bottom of the tube place a cotton wool plug covered with a circle of filter paper. Pour a suspension of floridin XXF in the solvent into the tube to form a column 2 to 5 cm. long after sedimentation, tapping the tube during this process. Pass through two column lengths of solvent not letting the floridin become dry. In one operation pour in a suspension of alumina in the solvent, tapping the tube during sedimentation. Cover the top of the adsorbent with a filter-paper disc and pass a column length of solvent, taking care not to dry out the column. The solvent flows under gravity; its linear velocity should be 2.5 to 4 mm. per min., and is controlled by the height of the bed of floridin.

Pass the solution (1 to 2 per cent.) of the azoyl methylglucitols through the column to form an initial band 3 to 5 mm. deep. Develop by passing solvent (20 to 30 column lengths) until the lower band reaches the bottom of the alumina column. Using benzene and alumina III, the 1 : 5-diazoyl-2 : 3 : 4 : 6-tetramethylglucitol remains at the top of the column in a sharp, intense band, while the trimethyl compound forms a diffuse band below. Using chloroform and alumina III, the upper band, at times diffuse, is in the middle of the column, while the lower band, sharp and intense, is at the bottom. When development is complete, pass two column lengths of light petroleum (b.p. 45° to 60° C.) and let the column dry for 15 min. Remove the different bands from the tube with a spatula and put each into a small tube plugged at the bottom with cotton wool. Elute the bands with acetone; elution is immediate and, with two washings, quantitative. Evaporate the eluate to dryness, and estimate the residue, dissolved in benzene, photometrically; crystallise from 98 per cent. ethanol and identify by a melting-point.

G. H. TWIGG

Polarographic Estimation of the Total Amount of Fat in Soaps and Soap Powders. S. Fiala and V. Jancik (*Coll. Czech. Chem. Comm.*, 1948, 13, 30-36)—The method is based on the principle that a soap solution will readily precipitate the cations of light and heavy metals by an exchange reaction with the alkali metal cations of the soap. If the concentration of these ions is measured polarographically before and after adding the soap,

the fat content of the soap can be calculated. Cadmium ions have been shown to be the most convenient for this purpose.

Procedure for solid soaps—Dissolve 10 g. of the soap in 100 ml. of 80 per cent. ethyl alcohol and neutralise the alkali present with 0.5 *N* hydrochloric acid, using phenolphthalein as indicator. After boiling the solution, neutralise the alkali liberated, and then dilute the solution accurately to 1 litre. Pipette 20 ml. of this solution into a 200-ml. volumetric flask containing 20 ml. of 0.25 *N* cadmium sulphate. After mixing the contents, add 20 ml. of saturated potassium chloride solution, dilute to 200 ml. with distilled water, and filter the solution. Examine a sample of the solution polarographically, after removing dissolved oxygen, and measure the height of the cadmium step produced. The percentage of fat in the soap is then given by

$$m(H - h) \times 10^6 / 198.85 H w N$$

where *h* is the height of the step given by this solution, *H* is the height of the step given by an exactly similar solution to which no soap has been added, *m* is the weight in milligrams of cadmium in 20 ml. of standard solution, *w* is the weight of soap in grams dissolved in 1 litre, and *N* is the neutralisation number of the fatty acids in the soap.

The cadmium sulphate stock solution should be stored free from carbon dioxide, and standardised gravimetrically as cadmium pyrophosphate.

To determine the neutralisation number of the fatty acids in the soap, shake 300 ml. of the soap solution with 10 ml. of 5.0 *N* hydrochloric acid and 30 ml. of ether. Wash the ether layer with water until the washings are neutral and filter the extract through anhydrous sodium sulphate into a dry, weighed flask. After removing the ether by evaporation, cool and weigh the flask and its contents. Dissolve the fat in 50 ml. of ethyl alcohol and titrate the solution with 0.5 *N* hydrochloric acid.

Procedure for soap powders—Dissolve 5 g. of the soap powder in 30 ml. of absolute alcohol, dilute the solution to 1 litre with alcohol, and filter through a filter paper. Pipette 20 ml. of the filtrate into a 200-ml. volumetric flask, and neutralise the alkali with 0.5 *N* hydrochloric acid. Add 100 ml. of water and 20 ml. of 0.25 *N* cadmium sulphate, followed by 20 ml. of saturated potassium chloride, and dilute to 200 ml. The subsequent procedure is the same as that described for solid soaps.

The results obtained by the above procedures are in good agreement with those given by other methods, and the method effects a considerable saving of time and materials. J. G. WALLER

Estimation of Residual Wool Fat in Tops Oiled with B.M. (Blended Mineral) Oil. E. W. Clark and W. L. Thomas (*J. Text. Inst.*, 1948, 39, T255-T259)—The method is based on the difference in the mean refractive indices of B.M. oil and wool fat, *i.e.*, 1.4707 and 1.4809, respectively, at 40° C.

Procedure—Extract 10 to 15 g. (accurately weighed) of the top with light petroleum (b.p. 40° to 60° C.), weigh the extract, warm it until it is thoroughly molten, and transfer some to the prism of an Abbé refractometer (maintained at

40° ± 0.1° C.). The wool-fat content is obtained from a graph or table (both reproduced in the original paper) relating the refractive index and percentage composition of the extract, and based on the refractive indices of known mixtures of B.M. oil and wool fat. [A condensed form of the table is given below.] The method is unaffected by the normal variations obtained in different batches of B.M. oil, or in wool fats from different wools, or by variations in temperature within the above limits. It can be adapted to oils other than B.M. oil by constructing an appropriate reference table or graph as described above. The method can be combined with the usual analytical process of solvent extraction, as 0.05 g. of extract suffices for a refractometer reading. The method is not applicable to tops combed in oil which have been stored for some time. This difficulty might be overcome by saponifying the extract, and determining the refractive index of the unsaponifiable matter, but a new reference table based on the appropriate standard mixtures would then have to be compiled.

Refractive indices at 40° C.	Percentages of wool fat in mixtures of B.M. oil and wool fat
1.4707	nil
1.4710	3.5
1.4720	14.8
1.4730	25.5
1.4740	36.0
1.4750	46.0
1.4760	56.0
1.4770	65.6
1.4780	75.0
1.4790	83.9
1.4800	92.5
1.4809	100.0

J. GRANT

Statistical Study of the Variables of Alpha-Cellulose Methods. A. S. O'Brien, L. K. Reitz, and R. C. Bloom (*Paper Trade J.*, 1948, 127, Aug., T.A.P.P.I. Sect., 51-54)—The analysis of variance

method applied to the determination of the α -cellulose contents of chemical cotton, high-alpha sulphite pulp, semi- and un-bleached krafts, and bleached sulphite wood pulps, led to the following conclusions. The correction for the moisture content of the sample must be determined with great care; preferably, the necessity to do so should be eliminated by the use of vacuum-dried pulp (dried at 60° C.). The method of rinsing with acetic acid, the size of the sample (1 or 3 g.), the amount of stirring during mercerisation, and the addition of the caustic soda in portions or all at once, have little or no influence on the results. The use of ground samples gives lower results than when thin sheets are used, and the use of alcohol and ether to hasten drying is not trustworthy. Dilution of the 17.5 per cent. caustic soda solution to 8.3 per cent., followed by an additional 1 hr. of standing before filtering (Amer. Chem. Soc. method), produced results slightly lower than those obtained by diluting to 8.3 per cent. with stirring, and then filtering at once (standard T.A.P.P.I. method

T203 m-44); either method gave results much lower than those obtained by filtering directly after treatment with the 17.5 per cent. caustic soda solution, without dilution. J. GRANT

Determination of Nicotine in Nicotine Sulphate and in Tobacco Leaves. G. Métayer (*Chimie Analyt.*, 1948, 30, 109-113)—Existing methods, which are reviewed, are time-consuming and require costly apparatus; they need the skill of qualified operators and some involve the use of inflammable solvents. The method now described is said to be free from these disadvantages.

Distillation apparatus—A 250-ml. Claisen flask with a Vigreux column in the side-arm is fitted with a rubber stopper bearing a 50-ml. tap funnel and an air inlet tube drawn off to a capillary at its lower end and fitted at the top with a rubber tube and screw-clip for regulation. This flask stands in an oil-bath. The receiver is a distillation flask closed with a stopper through which the side-tube of the Claisen flask passes to the centre of the receiver. The receiver is connected to a water-pump.

Procedure—Weigh 0.3 to 0.4 g. of nicotine sulphate or a quantity of tobacco dependent upon the approximate nicotine content, as follows: for tobacco containing 4 per cent. or more of nicotine, 1 g.; 2.7 to 4 per cent., 3 g.; less than 2.5 per cent., 5 g. Transfer the sample to the Claisen flask and add a quantity of potassium hydroxide pellets equal to the weight of nicotine sulphate or 2 per cent. of the weight of the tobacco sample. Add 110 ml. of ethylene glycol, reduce the pressure in the apparatus to 12 to 15 mm. and heat for 10 min. with the oil-bath at 120° to 140° C. to eliminate ammonia and readily volatile amines. Then raise the oil-bath temperature to 180° to 200° C. and distil 200 ml. of glycol at a steady rate while adding a further 120 ml. from the top-funnel. Efficient cooling is necessary. Transfer the contents of the receiver to a beaker, wash the receiver with water, add the washings to the distillate and dilute to 300 ml. with water. Titrate the nicotine with 0.05 N sulphuric acid to the neutral grey colour of an indicator prepared as follows. Dissolve 0.1 g. of methyl red in 7.4 ml. of sodium hydroxide solution [presumably 0.05 N], add 25 ml. of a 0.5 per cent. aqueous solution of methylene blue, and dilute to 500 ml.

The quantity of potassium hydroxide is specified as a result of experiments which showed that if the proportion was more or less than 2 per cent. of the weight of the (undried) sample of tobacco the results by the volumetric procedure were higher than those obtained by precipitating and weighing the nicotine as the dipicrate. [It is not indicated how the very small quantities of solid potassium hydroxide are to be weighed.]

The method gives results in good agreement with those obtained by the method of Schloesing (*Cours de Chimie analytique*, Paris, 1913). Only one type of tobacco, Nijkerk, was found not to be amenable to the procedure, but this variety gives difficulties in other methods. W. C. JOHNSON

Analytical Method for the Examination of Technical Polyvinyl Products. W. J. Taat and W. van der Heul (*Chem. Weekblad.*, 1948, 44, 393-397)—The usual methods for the examination of polyvinyl products take several days, and are unable to distinguish a co-polymer from a mixture of polyvinyl acetate and chloride. The new method is based on the solvent power of *o*-dichlorobenzene, and it is essential that this solvent shall be free from non-volatile compounds. This is ensured by using the fraction of the commercial material boiling between 155° and 183° C.

Procedure—Cut the sample, freed from fabric, into pieces, and dissolve 0.5 g. in 15 ml. of *o*-dichlorobenzene with the aid of gentle heat. Add to the solution 30 ml. of butanone, and centrifuge. Pour off the liquid, wash the residue twice with a mixture of *o*-dichlorobenzene and butanone, and dry it at 105° C. to constant weight. This gives the weight of filler or pigment. Evaporate the solution and wash liquors on the water-bath to 30 ml. and add 100 ml. of warm, 96 per cent. alcohol. After the mixture has been kept for 1 hr. on the water-bath, filter it on a glass filter IH3, and wash the residue with 96 per cent. alcohol. Dry the residue at 100° C., and weigh it. This gives the weight of polyvinyl chloride and/or chloride-acetate co-polymer. An estimation of chlorine is carried out on this mixture to determine the proportions of the two components. Evaporate the filtrate from the last coagulation on the water-bath to constant weight; redissolve it in 80 ml. of acetone and add 40 ml. of water. Filter off the coagulum, wash with 50 per cent. acetone, and dry. This is the polyvinyl acetate. Evaporate the filtrate and dry at 80° C. to give the weight of plasticiser.

G. MIDDLETON

Inorganic

Rapid Estimation of Free Sulphur. L. Peyron (*Bull. Soc. Chim.*, 1948, 482-483M)—The general principle of the method is said to be capable of extension to the estimation of other substances. It consists in dissolving the substance in a liquid and mixing the solution with another liquid in which the substance is insoluble, so that a colloidal dispersion is obtained. The opacity or refractive index of the dispersion is then determined as a measure of the concentration of the substance.

Procedure—Heat the sample, containing about 5 mg. of sulphur, with 5 ml. of pure pyridine at 60° C. for 1 hr. with occasional shaking. Filter and add 1 ml. of the filtrate, dropwise with shaking, to 10 ml. of water. Determine the opacity with a suitable optical or photo-electric instrument and interpret the results from a calibration curve based on known amounts of sulphur treated in the same manner. Reference dispersions of sulphur must be renewed after 2 to 3 hr. Bituminous samples must first be treated with a solvent that has no action upon the sulphur. W. C. JOHNSON

Semi-micro Determination of Halogens and Sulphur [and Mercury] in Substances containing Mercury. M. Jurecek (*Coll. Czech. Chem.*

Comm., 1947, 12, 455-466)—Sodium carbonate at a low red heat is a satisfactory absorbent for chlorine, bromine, and sulphur when the mercury compound is heated in a current of oxygen. Iodine is not completely absorbed by sodium carbonate and for compounds containing this element silver dispersed in magnesium oxide must be used. The mercury vapour passes on and can be determined by absorption on gold wool, but if nitrogen is also present, mercury must be determined separately by combustion with oxidising agents in an indifferent gas.

Apparatus—(a) Supremax glass combustion tube, length 45 cm., internal diameter 10 mm., wall thickness 0.7 to 1 mm., with neck. When mercury is to be determined, a transparent fused quartz tube, of the same dimensions but with a ground-on absorption tube in place of the neck, is used. The straight part of the absorption tube is 5 cm. long, 5 mm. in diameter, and filled with gold wool. (b) Platinum contact star, length 5 cm. (c) Glazed porcelain boat, 6 cm. long and occupying two-thirds of the section of the tube. (d) Hard glass "ampoule," with loop, 9 mm. diameter, 5 cm. long, which is placed near the mouth of the tube to prevent the substance from subliming back. (e) Three sheet-iron heating mantles, 10, 6, and 4 cm. long, respectively. (f) Mariotte bottle, 3-litre capacity. (g) Bubble counter, calibrated by means of (f).

Special reagents—(a) Silver dispersed in magnesium oxide: mix magnesium oxide to a paste with a solution of an equal weight of silver nitrate, evaporate the water on a water-bath, heat on an asbestos mat until no more brown vapours are evolved, and finally ignite at red heat. (b) Mercuric nitrate solution, 0.04 *N*: dissolve 4.4 g. of mercuric oxide in the smallest quantity of diluted nitric acid (1 + 1) and dilute with water to 1 litre. Determine the factor of this solution against 3- to 8-ml. quantities of 0.04 *N* sodium chloride diluted to 40 ml., acidified with 2 drops of nitric acid and containing 0.01 g. of sodium nitroprusside. Titrate with the mercuric nitrate solution to the production of an opalescence that lasts 1 min. To determine the factor on 0.04 *N* potassium bromide proceed similarly, but dilute to 60 ml. (c) Sodium hypochlorite solution: introduce 7 g. of chlorine into 100 ml. of 12 per cent. sodium hydroxide solution.

Determination of chlorine, bromine, and sulphur—Insert the porcelain boat, filled with anhydrous sodium carbonate, into the combustion tube to a distance of 10 cm. from the neck. Boil the platinum star with diluted nitric acid (1 + 1), ignite it gently and insert it in the tube 1 cm. from the boat. At a further interval of 5 to 8 cm. place a platinum boat containing 20 to 30 mg. of the substance for analysis and then, at a distance of 4 cm., the "ampoule." Close the tube temporarily with a plug of cotton wool, arrange the 10-cm. and 6-cm. heating mantles, in contact, to cover respectively the porcelain boat and the star and thus to extend about 3.5 cm. beyond the boat. Adjust the 4-cm. mantle between the platinum boat and the "ampoule." Replace the cotton wool plug with a rubber stopper through which passes the capillary of the bubble counter, which

is connected in turn with an oxygen holder or cylinder with a fine regulator valve. Arrange a shield over the part of the tube containing the porcelain boat and the star, to conserve the heat. Regulate the oxygen at 7 to 9 ml. per min. heat the mantle over the star to a bright red with a double Bunsen burner, and that over the boat of sodium carbonate to a dull red with a 7-cm. burner, then light a Bunsen burner under the third mantle and ignite the substance in the usual manner, advancing the burner and the mantle toward the star. The combustion should occupy 45 min. The mercury forms droplets on the cold tube beyond the porcelain boat; any white crystalline sublimate indicates that the combustion has been too rapid. Having advanced the short mantle to touch the central one, extinguish the burners and allow the apparatus to cool with the oxygen still passing. Transfer the contents of the porcelain boat to a 100-ml. flask, add water and 1 ml. of concentrated nitric acid and dilute to 40 ml. for a chloride titration or 60 ml. for a bromide titration. Using sodium nitroprusside as indicator titrate with 0.04 *N* mercuric nitrate to the production of an opalescence lasting 1 min. Bromine can be titrated separately as follows. Dissolve the sodium carbonate from a second combustion in 20 ml. of water in a 250-ml. Erlenmeyer flask with a ground-glass stopper, neutralise to methyl red with *N* hydrochloric acid, and make alkaline with 1 drop of *N* sodium hydroxide. Add 5 ml. of sodium hypochlorite solution and 2 g. of sodium chloride, and pass a current of carbon dioxide for 15 min. Heat over boiling water for 10 min., add 5 ml. of 10 per cent. sodium formate solution and some glass balls, and boil for 15 min. Cool, acidify with 25 ml. of 2 *N* sulphuric acid, add 1 to 2 drops of 5 per cent. ammonium molybdate solution and 1 to 2 g. of potassium iodide, stopper, and allow to stand for 5 min. Titrate the liberated iodine with 0.1 *N* sodium thiosulphate and starch as indicator. Determine sulphur as barium sulphate by the usual procedure.

Determination of iodine—Follow the above procedure but fill the porcelain boat with silver dispersed in magnesium oxide. After the combustion, dissolve the absorbent in 5 ml. of diluted nitric acid (1 part of acid, sp.gr. 1.4 + 2 parts of water). Dilute with 25 ml. of water, boil for 10 min., allow to cool, collect the silver iodide in a 12G4 filter tube, dry in a Pregl copper block, and weigh.

Simultaneous determination of halogens, sulphur, and mercury in substances containing no nitrogen—Follow the procedure for chlorine and bromine or iodine but use the quartz tube with the weighed absorption tube in place. The gold is kept cool by a piece of cloth, which is moistened from time to time. Having completed the combustion, extinguish the movable burner and that under the platinum star and increase the oxygen current to 12 to 15 ml. per minute. Move back the 10-cm. mantle by 3 cm. and place the full flame of a micro-burner 3 cm. behind the deposit of mercury. Extinguish the burner under the porcelain boat and advance the micro-burner at 3 mm. per minute to within 1 cm. of the gold wool. Repeat once or twice the

heating of the tube between the boat and the gold, and allow to cool in the current of oxygen. Detach the absorption tube and attach to its ground end a calcium chloride tube, attach the other end to the Mariotte bottle and draw 300 to 500 ml. of air through the tube at about 15 ml. per minute. After weighing, remove the mercury, in preparation for the next determination, by careful ignition and cooling while maintaining a current of dry air.

W. C. JOHNSON

Separation and Determination of Fluorine.
E. Rinck (*Bull. Soc. Chim.*, 1948, 305-324M)—A comprehensive and critical review of published methods, some of which are also re-investigated by the author. [This abstract deals only with the author's contributions and with the methods he favours.]

Gravimetric methods—Precipitation as calcium fluoride by a method quoted from *Handbuch für das Eisenhüttenlaboratorium*, 1939, 1, 17, 134, 153, gives results from 0.44 to 0.70 per cent. low. The method is considered satisfactory, although owing something to a compensation of errors. Precipitation as lead chlorofluoride with suitable precautions (Fischer and Peisker, *Z. anal. Chem.*, 1933, 95, 225) is accurate to within 0.3 per cent., but the volumetric development (*infra*) of this method is preferred.

Volumetric methods—The direct titration of chloride in precipitated lead chlorofluoride offers no advantage over the gravimetric method, but the following indirect method is recommended as accurate to within 0.5 per cent.

The fluoride solution must contain less than 100 mg. of fluorine in not more than 200 ml. and must be free from chloride. Neutralise the solution to methyl orange and add a known volume of 0.1 N sodium or potassium chloride. Add, drop by drop, a slight excess of 0.1 N lead nitrate to the hot solution and set aside for 12 hr. Check for neutrality, transfer the solution and the precipitate to a standard 250- or 500-ml. flask and dilute to the mark. Filter through a dry paper, rejecting the first portions and, to an aliquot of not more than 40 ml., add 10 ml. of a freshly prepared solution of diphenylamine blue. Titrate with 0.1 N silver nitrate, with vigorous agitation, until a permanent violet tint is obtained. The indicator is prepared by adding 0.1 ml. of a solution of 1 g. of diphenylamine in 100 ml. of sulphuric acid and 1 ml. of 0.1 N potassium dichromate to 10 ml. of 5 N sulphuric acid.

Titration with neutral *M/16* aluminium chloride of fluoride or silicofluoride solutions saturated with sodium chloride, in presence of methyl red as indicator (Kurtenacker and Jurenka, *Z. anal. Chem.*, 1930, 82, 210), is strongly recommended. In absence of interfering ions the error is less than 0.5 per cent. Sulphate, in concentration equal to that of the fluorine ion, causes the results to be 3 per cent. high. Perchlorate gives a 1 per cent. error at the same concentration. Carbonate causes large errors; for this reason the aluminium chloride solution must be protected with a soda-lime tube

and the evaporation of alkaline fluoride solutions must be avoided.

Titration with thorium nitrate in the presence of sodium alizarin sulphonate (Willard and Winter, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 7) is the best method. The present author's experiments give rise to the following observations and recommendations: (a) The most satisfactory end-points are obtained when 1 mg., or less, of fluoride is titrated; then the thorium fluoride remains in colloidal solution. With larger quantities, the rose-coloured lake that marks the end-point is adsorbed on the precipitated fluoride. (b) 0.01 Mg. of fluoride in 30 ml. of solution can be determined to within 0.001 mg. (c) The maximum volume of solution recommended is 50 ml., preferably 25 to 30 ml., for quantities down to 0.01 mg. The colour is highly dependent on the indicator concentration; the volume of the solution should not, therefore, increase by more than 10 per cent. during the titration. (d) Thorium nitrate solution: maximum concentration, 0.05 N; recommended, 0.01 N (= 0.0025 M), used in a micro-burette graduated in 0.01 ml. (e) Indicator solution: 1 g. of sodium alizarin sulphonate in 1 litre of water. Add 1 drop to 10 ml. of solution. (f) The end-point is best observed in diffuse daylight. It should be the same colour as that obtained in standardising the thorium nitrate, but a comparison solution thus prepared rapidly becomes deeper in colour. The cobalt nitrate-sodium dichromate standard tint of Matuszak and Brown (*Ind. Eng. Chem., Anal. Ed.*, 1945, 17, 100) does not provide an identical colour, especially when variable concentrations of fluoride and of other ions modify the colour of the end-point, but the standard proves useful with practice. (g) Aqueous solution is better than the 50 per cent. alcoholic solution used by Willard and Winter (*loc. cit.*) except for about 0.1 mg. of fluoride, which is more precisely titrated in dilute alcohol. The presence of alcohol does not affect the proportionality between the quantity of fluoride and the volume of thorium nitrate solution required (*cf. Dahle et al., J. Assoc. Off. Agric. Chem.*, 1938, 21, 459, 468). (h) The pH at the end-point should be 3.6 to 3.9 for alcoholic solutions and this may be achieved by using a chloroacetate buffer (Hoskins and Ferris, *Ind. Eng. Chem., Anal. Ed.*, 1936, 8, 6), although the latter must be freshly prepared, otherwise hydrolysis products diminish the pH. Contrary to the findings of the original authors, the F : Th relationship is constant under these conditions. In aqueous solutions the correct pH of 3.25 to 3.45 at the end-point is attained by adjusting the original solution to a pale rose colour with hydrochloric acid or sodium hydroxide and then adding 1 drop of 2 to 3 per cent. acetic acid. An excessive concentration of acetate ions renders the end-point less sharp. The use of a solution of thorium nitrate in 1.2 N acetic acid (Matuszak and Brown, *loc. cit.*) leads to a lack of proportionality between fluoride and thorium. (i) The quantity of thorium nitrate solution required to form the lake in a blank experiment must be deducted from each titration.

Colorimetric methods—The zirconium nitrate-sodium alizarin sulphonate method of De Boer and Basart (*Z. anorg. Chem.*, 1926, **152**, 203) is the most useful.

Separation of fluoride from interfering substances by distillation—The author recommends the method of Willard and Winter (*loc. cit.*), but uses a separate steam generator. Sulphuric acid at 155° to 160° C. or perchloric acid at 140° to 145° C. may be employed, but the latter is preferable since any sulphuric acid that may be entrained has a severe influence on certain methods of determination, notably the thorium nitrate titration (Hoskins and Ferris, *loc. cit.*). A mixture of equal volumes of sulphuric acid and 72 per cent. perchloric acid may be employed for minerals more easily decomposed by sulphuric acid. The use of phosphoric acid is deprecated, since it is readily entrained and has a strong influence on the subsequent titration. If phosphate is present in the substance for analysis the distillation should be repeated, the second time at a temperature not higher than 135° C. The rate of distillation is without influence, apart from the risk of entrainment, if too rapid. Quantities of fluorine of the order of 1 mg. may be recovered completely in 100 ml. of distillate in 15 to 20 min., even from insoluble fluorides. Gelatinous silica retards the distillation of the hydrofluosilicic acid. If the SiO₂ : F ratio is 20 : 1, 300 ml. of distillate must be taken; if the ratio is 50 : 1, 400 ml. of distillate are necessary. A greater ratio necessitates a preliminary separation. Ferric and ferrous ions also retard the distillation. Aluminium should be separated prior to the distillation when it is present in more than ten times the fluorine concentration. The suitability of the reagents and of the glassware must be checked by a blank distillation and titration. Pyrex glass has been found to lead unaccountably to high results.

Evaporation of solutions of alkali fluorides—Reynolds and Hill (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 21) and McClure (*Ibid.*, 1939, **11**, 171) found that losses occurred when solutions of alkali fluorides were evaporated. This is confirmed, but the reason is not discovered. Evaporation should be avoided, or if this is not possible the pH should be kept at 6 to 8 and a platinum or Jena glass vessel should be employed. Absorption of carbon dioxide even by a neutral solution rules out subsequent titration with aluminium chloride.

W. C. JOHNSON

Colorimetric Method for Determining Fluoride Ions in Presence of Phosphates. D. Monnier, R. Vaucher, and P. Wenger (*Helv. Chim. Acta*, 1948, **31**, 929-932)—When the bleaching effect of fluoride ions on pertitanic acid is employed for the colorimetric estimation of fluoride, the pH and the concentration of peroxide must be strictly controlled.

Solutions—Place 26.7 ml. of an 18 per cent. solution of titanous chloride in a litre measuring flask, dilute with a small volume of boiled water, add 100 ml. of concentrated sulphuric acid and 60 ml. of perhydrol, and fill to the mark with boiled distilled water. This solution may be kept

for several months. For use, dilute it ten-fold. Prepare a standard fluoride solution containing 1.947 g. of ammonium fluoride in 1 litre and dilute this solution 100-fold to obtain a solution containing 0.01 mg. of fluoride per ml.

Procedure—Measure 7.5 ml. of 1.2 N hydrochloric acid, 3 ml. of the reagent solution, and 1 ml. of perhydrol into a 50-ml. flask, and dilute to the mark. Measure the optical density of this solution by means of the Hilger Spekker absorptiometer with a 4-cm. cell, filters H503 and Ilford 601, and the tungsten filament lamp. Repeat the procedure, adding increasing quantities of the diluted fluoride solution before the final dilution, and construct a calibration curve.

The curve follows the Beer-Lambert law for quantities of fluoride from 30 to 160 µg. per 50 ml. of solution. The method is not very sensitive, the molecular extinction coefficient being 163. The maximum error is about 3 µg. of fluoride.

Estimation of fluorine in teeth—In order to preserve the correct conditions it is necessary to vary the quantity of acid according to the type and quantity of the sample, as follows.

Finely powdered substance	Quantity in g.	1.2 N HCl in ml.
Enamel	0.3	12
"	0.1	9
"	0.05	8.5
"	0.01	8
Dentine	0.3	10.5
"	0.1	8.5
"	0.05	8
"	0.01	8
Entire tooth	0.3	11.5
" "	0.1	9
" "	0.05	8.5
" "	0.01	8

Mix the prescribed quantity of acid with 3 ml. of the reagent solution, pour the mixture on to the sample, wash the mixing vessel with 10 ml. of water, and add this to the reaction mixture. Allow the reaction to proceed for not more than 10 min. with occasional stirring. Transfer to a 50-ml. measuring flask, add 1 ml. of perhydrol to compensate for any reduction due to organic matter, and make up to the mark. Filter through two dry papers, check the complete clarity of the filtrate, measure its light absorption, and read the fluorine content from the calibration graph. W. C. JOHNSON

Determination of Silver with Ascorbic Acid. E. C. Stathis (*Anal. Chem.*, 1948, **20**, 271)—**Procedure**—Weigh a sample containing not more than 0.1 g. of silver, and treat it with 5 ml. of 6 N nitric acid; then evaporate the solution almost to dryness on the steam-bath. Dilute to 20 ml. with distilled water and heat the solution to between 90° and 100° C. before adding slowly 10 ml. of freshly prepared, 2 per cent. ascorbic acid solution. Maintain at this temperature for 15 min., then filter the precipitate of metallic silver on to a porcelain filter crucible, wash it with hot water, and ignite it.

Results—On 10 samples containing from 11 to 138 mg. of silver the maximum error was 0.2 mg. Lead, copper, bismuth, cadmium, nickel, and zinc do not interfere.

M. E. DALZIEL

New Conductometric Method for the Titration of Univalent Thallium using Potassium Selenocyanate. R. Ripan and E. Popper (*Gazz. Chim. Ital.*, 1942, **72**, 439–445)—Thallium acetate can be titrated conductometrically, potassium selenocyanate being used as precipitant.

Procedure—The titre of the solution of selenocyanate was determined potentiometrically with silver nitrate and volumetrically using fluorescein as indicator. The solution of thallium acetate was titrated conductometrically with potassium chromate and with potassium iodide for comparison with the results with the selenocyanate. The thallium salt, which should be neutral or slightly alkaline, is placed in the titration cell and the reagent added slowly with continual stirring. Thallium selenocyanate separates immediately as a crystalline precipitate that settles rapidly leaving the solution perfectly clear. Equilibrium is immediately established after each addition so that the reading can be made at once, giving the advantage of rapidity in working. During the precipitation the conductivity changes very little, but when quantitative precipitation has been attained the conductivity increases rapidly and the two branches of the curve intersect at an angle sufficiently acute to permit great precision. For the most accurate results the concentration of the thallium acetate should be about 0.025 *M* and that of the selenocyanate about 0.5 *M*.

The results obtained are in close agreement with those found with potassium chromate or potassium iodide.

The inverse titration, using the thallium salt as reagent, is less precise, the angle between the two branches of the curve being much greater.

A. H. BENNETT

Critical Study of the Gravimetric Determination of Calcium in Presence of Magnesium. S. Peltier and C. Duval (*Analyt. Chim. Acta*, 1947, **1**, 408–417)—Published procedures for the gravimetric determination of calcium have been investigated to establish which methods are suitable for use in presence of large quantities of magnesium. The methods studied included precipitation as oxalate in various ways, precipitation as tungstate, molybdate, or sulphate (from alcoholic solution), and also the use of 8-hydroxyquinoline for removal of magnesium before determining the calcium. The precipitations were carried out with chloride solutions containing 10 to 40 mg. of calcium and, at least, 20 times that weight of magnesium.

The use of 8-hydroxyquinoline for preliminary separation of the magnesium gave low results owing to entrainment of calcium with the oxine precipitate. The procedure that gave satisfactory results with a single precipitation were (i) precipitation of calcium as tungstate, (ii) precipitation as oxalate in the cold in presence of glycerol, (iii) precipitation as oxalate at pH 3.7 in presence of formic acid,

and (iv) precipitation as sulphate from 60 per cent. alcohol solution (re-precipitation as oxalate is recommended). Precipitation as molybdate is unsatisfactory (*cf.* Iwin and Grinstein, *Z. anal. Chem.*, 1944, **127**, 20). The tungstate procedure is recommended for its speed and ease of execution.

Determination of calcium in presence of magnesium (tungstate method)—Adjust the solution, of volume about 70 ml. and containing about 0.035 g. of calcium ion, to pH 7 to 8 and heat to 80° C. Add 2 ml. of 19 per cent. sodium tungstate solution and stir, without touching the walls of the containing vessel, until precipitation is complete. Allow to cool and, after 30 min., filter the precipitate on a weighed, No. 3 sintered-glass crucible, washing with 20 ml. of hot water. Dry for 1 hr. at 110° C., cool, and weigh.

The precipitation should be carried out in a solution containing only calcium, magnesium, and alkali metals. Large amounts of ammonium chloride prevent the precipitation. H. J. CLULEY

Determination and Separation of Calcium and Magnesium. A. Lassieur (*Chimie Analyt.*, 1947, **29**, 197–201)—Methods for determining calcium and magnesium in presence of one another and in presence of lithium are described.

DETERMINATION OF CALCIUM IN PRESENCE OF MAGNESIUM—Using bromophenol blue as indicator, adjust to pH 4 to 4.5 a solution containing not more than 1.5 g. of calcium oxide and 0.5 g. of magnesium oxide per litre and occupying a volume of about 300 ml. Heat to boiling and add 2 g. of solid ammonium oxalate; continue to boil for 2 min. Filter immediately and wash the paper and precipitate with warm water. Ignite and weigh as calcium oxide.

Serious contamination of the calcium oxalate by magnesium occurs if the precipitate is allowed to stand in the cold before filtration. A satisfactory separation can be made in presence of alkali salts without the need for re-precipitation.

DETERMINATION OF MAGNESIUM—Lithium absent—To the filtrate from the calcium oxalate precipitate add an excess of ammonium dihydrogen phosphate, followed by 5 ml. of aqueous ammonia in excess. Stir to promote the crystallisation of the magnesium ammonium phosphate. If precipitation occurs almost immediately, allow to stand for 4 hr. before filtering, otherwise set aside for 16 hr. Collect the precipitate on a suitable filter, wash with diluted aqueous ammonia (1 in 10) and ignite at a red heat and weigh.

Addition of 5 g. of ammonium chloride is without effect.

Lithium present—Lithium is co-precipitated with magnesium on adding ammonium phosphate, as is shown by the flocculent nature of the precipitate, and must be separated as follows. Dissolve the precipitate in hydrochloric acid, add ferric chloride equal to 20 times the weight of phosphates present, and precipitate the iron with aqueous ammonia, at the boiling-point. Filter, evaporate the filtrate to dryness, and ignite. Extract the residue with acetone, which dissolves the alkali chlorides present, leaving the partially decomposed magnesium

chloride undissolved. Filter, re-dissolve the residue in acid and precipitate the magnesium with ammonium phosphate by the procedure already described.
P. M. C. PROFFITT

New Volumetric Method of Determining Mercuric Oxide with Alkali Thiocyanate. F. Burriel and F. Pino (*Informac. Quim. Analit.*, 1947, 1, 46-49, 68)—The determination is based on the reaction

$$4\text{KCNS} + \text{HgO} + \text{H}_2\text{O} \rightarrow \text{K}_2[\text{Hg}(\text{CNS})_4] + 2\text{KOH}$$

and is a modification of the Büllmann-Thanlow method (*Bull. Soc. Chim.*, 1921, (4), 29, 587) in which potassium iodide is used.

Procedure—Treat 0.1 to 0.2 g. of the sample in an Erlenmeyer flask with 15 g. of potassium thiocyanate and enough water to give a volume of 100 ml. Keep the flask stoppered to prevent absorption of carbon dioxide, and if necessary warm to effect dissolution. Cool, and titrate the liberated potassium hydroxide with 0.1 N sulphuric acid, using as indicator methyl orange or the screened methyl red-methylene blue indicator; 1 ml. of 0.1 N sulphuric acid is equivalent to 0.01083 g. of mercuric oxide. A. F. STURGESS

Cerimetric Determination of Copper and Antimony. R. Příbil and T. Chlebovsky (*Coll. Czech. Chem. Comm.*, 1947, 12, 485-501)—

The copper, in 5 to 6 N hydrochloric acid solution, is reduced to the univalent state by means of a solution of chromous chloride. The slight excess of chromous chloride is removed and the copper is titrated with a standard solution of ceric sulphate. The reactions are conducted in a closed titration vessel in an atmosphere of carbon dioxide and the end-points are detected potentiometrically, a platinum spiral as indicator electrode and a calomel reference electrode being used. Nickel, cobalt, manganese, zinc, lead, antimony, and arsenic do not interfere, but iron is titrated with the copper. In a solution containing 40 ml. of concentrated hydrochloric acid and 20 ml. of concentrated sulphuric acid in each 100 ml. both copper and antimony can be determined. The solution is reduced as above and the copper is titrated; iodine chloride solution is then added to act as a catalyst in the oxidation of the antimony by the titrant.

The original paper should be consulted for discussion of the experimental development of the method and for further details of the determination of copper in alloys, and the determination of copper, antimony, and arsenic in alloys with lead and tin.
L. A. DAUNCEY

Systematic Analysis of Cations by the Polarographic Method. II. Conditions for Determining Elements of the Arsenic Sub-Group. M. A. Portnov and V. P. Povelkina (*J. Anal. Chem. Russ.*, 1948, 3, 85-91)—*Tin*—With barium chloride or sodium chloride as supporting electrolyte, concentrations of stannous tin from 0.0008 to 0.02 N in N hydrochloric acid, obtained by dissolution of tin in 6 to 8 N hydrochloric acid, followed by dilution and passage of hydrogen gas

for 1 hr., gave wave-heights proportional to concentration. In diluted sulphuric acid or in 10 per cent. sodium hydroxide solution, proportionality occurred only with tin concentrations not less than 0.003 N (reduction potential, about -0.4 v.), but in the alkaline solution indications, not further investigated, of two unstable waves were obtained. In a mixture of equal volumes of 5 N sulphuric acid and ethyl alcohol, with sodium or potassium sulphate as supporting electrolyte and in an atmosphere of hydrogen, wave-heights were strictly proportional to tin concentration over the range 0.0004 to 0.0054 N. With stannic tin in hydrochloric acid solution, the wave-height slowly decreased with time.

Antimony—Conditions given by Suchy (*Chem. News*, 1931, 143, 213) and Cozzi (*Annali Chim. Appl.*, 1934, 442, cf. also Lingane, *Ind. Eng. Chem., Anal. Ed.*, 1943, 15, 583) for determining antimony in hydrochloric acid medium were found satisfactory. In 10 N sulphuric acid, antimony is reduced at -0.2 v., and wave-heights were proportional to concentration. In oxalic acid medium, trivalent antimony is reduced at -0.4 v., and proportionality was also found. In 10 to 20 per cent. sodium hydroxide solution, the reduction potential is -0.2 v., but proportionality occurred only at concentrations of 0.006 N and above. In neutral solution, the reduction potential is -0.6 v. In a 1 : 1 mixture of 5 N sulphuric acid and ethyl alcohol the reduction potential is -0.27 v., and proportionality between wave-height and concentration occurred over the range 0.00036 to 0.0058 N, but with concentrations below 0.0007 N two waves tended to form. For the determination of antimony in this medium the total wave given by a solution containing gelatin and sodium or potassium sulphate as supporting electrolyte, and freed from oxygen by means of hydrogen, should be measured.

Arsenic—In alkaline medium, arsenic is not reduced at the dropping mercury electrode. In sulphuric acid solution three waves appeared, the first two only could be used for analytical work since the third is unstable. In alcoholic sulphuric acid solution (see above), three waves with half-wave potentials, -0.64, -0.88, and -1.15 v. appeared. With the first of these waves, concentration and wave-height were proportional over the range of arsenic concentration 0.00030 to 0.0025 N.

Determination of tin, antimony, and arsenic when present together—In 0.5 N sulphuric acid well defined waves of all three elements, with two of the arsenic waves missing, appeared, but the wave-heights of antimony and tin were not proportional to their concentrations. In more concentrated sulphuric acid solutions the reduction potential of the "stable" arsenic wave became more positive and the wave coalesced with that of tin. In alcoholic sulphuric acid solution (see above) in presence of gelatin, results for each of the three elements present together were satisfactory provided the polarograms were taken without delay after the preparation of the solution. Furthermore, lead, which accompanies the arsenic group elements in certain methods of

analysis, did not interfere, and there was no need to filter off the lead sulphate before the electrolysis.

G. S. SMITH

Determination of Alumina in Silica Bricks by Precipitation with 8-hydroxyquinoline
T. R. Lynam and A. Nicholson (*Trans. Brit. Ceramic Soc.*, 1948, **47**, 116-119)—Cashmore and Cowling (*Ibid.*, 1946, **45**, 309) proposed for determining alumina in clays and firebricks a rapid method in which the alumina is precipitated with 8-hydroxyquinoline from a buffered aqueous extract of a sodium hydroxide fusion of the sample. This method cannot be applied to the determination of alumina in silica bricks, the precipitation of the aluminium oxinate being partly or wholly suppressed. Determinations on synthetic silica-alumina mixtures showed that the silica-alumina ratio is a critical factor, incomplete precipitation of the alumina occurring with ratios greater than 20 : 1. For the analysis of silica bricks and other highly siliceous materials, the preliminary removal of silica with hydrofluoric acid is recommended.

Procedure—To 1 g. of the finely-ground sample add 5 drops of sulphuric acid and 8 ml. of hydrofluoric acid, evaporate to dryness, and ignite. Fuse the residue with 6 to 8 g. of sodium carbonate, extract the cold melt with boiling water, filter, and wash with hot water. To the filtrate add hydrochloric acid dropwise until the solution is acid to methyl orange, boil for 2 min., and cool. To eliminate interference from any iron present, add 1 ml. of 50 per cent. hydroxylamine hydrochloride solution and 20 drops of 1 per cent. *o*-phenanthroline in diluted hydrochloric acid (1 + 1) solution. Add 15 ml. of 2.5 per cent. 8-hydroxyquinoline in 5 per cent. acetic acid solution, heat to 70° C., add 30 per cent. ammonium acetate solution until a permanent precipitate results and then add 10 ml. more. Allow to stand for 10 min. and filter through a pulp pad, washing with water. Redissolve the precipitate through the pad with 75 ml. of nearly boiling, diluted hydrochloric acid (1 + 1), and wash with hot water. Transfer the solution to a flask provided with a stopper, dilute to 200 ml., and cool.

Add standard bromate-bromide solution (1 ml. \equiv 1 mg. Al_2O_3) from a burette, slowly and with constant shaking. When 5 ml. short of expected requirements have been added, add 3 drops of 1 per cent. indigo carmine solution and continue titrating until the green colour disappears. Add 3 more drops of indigo carmine solution, titrate to a golden-yellow colour, and add 3 ml. more of bromate-bromide solution. Stopper the flask, shake well, and allow to stand for 5 min. Add 10 ml. of 20 per cent. potassium iodide solution and titrate back with standard sodium thiosulphate solution, using starch solution as indicator. H. J. CLULEY

Volumetric Determination of Tervalent Iron Based on the Use of Tartrates. A. V. Pavlinova (*J. Anal. Chem. Russ.*, 1948, **3**, 7-10)—A solution of ferric chloride, neutralised to methyl orange, yields on treatment with sodium potassium tartrate

solution, also neutralised to methyl orange, an amount of acid, as measured by titration to the phenolphthalein end-point, that is proportional to the iron content of the solution, provided hydrolysis is prevented by adding calcium chloride. Tests showed that 0.0189 g. of iron combine with tartaric acid equivalent to 0.0656 g. of sodium potassium tartrate. Thus the complex contains the iron and the tartrate residue in the molecular proportions of 4 : 3. Titration of the acid liberated showed that three equivalents are formed for each equivalent of iron. The amount of calcium chloride necessary to yield theoretical results was the equivalent of not less than 0.4 ml. of 40 per cent. (half-saturated) calcium chloride solution for each 20 ml. of solution. Titration of the calcium chloride solution alone showed that 1 ml. required 0.06 ml. of 0.1 *N* potassium hydroxide for neutralisation to phenolphthalein, but tests with various amounts of the solution added to a ferric tartrate solution showed that a correction based on this figure was faulty. The results were identical when the final concentration of calcium chloride was between the limits of 0.5 and 2 per cent.

Procedure—To 20 ml. of ferric chloride solution, neutral to methyl orange and containing 0.1890 to 0.05670 g. of iron [this was the range in the experiments], add 2 or 3 ml. of 10 per cent. sodium potassium tartrate solution, and 2 drops of phenolphthalein indicator solution, and titrate with 0.1 *N* potassium hydroxide, free from carbonate, until the solution, after becoming nearly colourless, turns pink. Then add 0.5 to 1 ml. of 40 per cent. calcium chloride solution and titrate the now decolorised solution to the final end-point at the rate of 1 or 2 drops per 15 sec.

The maximum errors were +0.42 and -0.35, and the average error ± 0.20 parts in 100.

A similar method has been used by the author for determining aluminium. G. S. SMITH

Determination of Oxidic Inclusions in Steel.
H. Henkel (*Z. anal. Chem.*, 1947, **128**, 26-41)—Klinger and Koch (*Arch. Eisenhüttenw.*, 1937-38, **11**, 571) have described a procedure for the determination of oxidic inclusions in steel, in which a preliminary separation of the inclusions is effected by an electrolytic method. Experience of this procedure has led the author to suggest a number of modifications, including a preliminary heat treatment to reduce to a minimum the amount of carbide present in the sample. This facilitates the separation of the inclusions and minimises the danger of iron carbide remaining unchanged during the subsequent treatment of the inclusions and thus giving rise to high values for ferrous oxide. A further modification is the use of a gravimetric method for determining silica, which is claimed to give more trustworthy results than the absorptiometric silicomolybdate procedure recommended by Klinger and Koch.

Apparatus—The electrolytic separation of the inclusions is carried out in the apparatus described by Klinger and Koch (*loc. cit.*). The anodic compartment is fitted with a filter and a circulating

system for the anolyte. The catholyte is contained in a porous pot treated with agar-agar, which acts as a diaphragm. The anolyte contains 150 g. of sodium citrate, 18 g. of potassium bromide, and 2 g. of potassium iodide per litre, and the catholyte is 10 per cent. cupric bromide solution. The sample, which is made the anode, is rotated mechanically during the electrolysis.

Preparation of the samples—Two samples, of weight 60 to 80 g. and length 8 to 10 cm., are required for each complete determination. Stamp the samples for identification and carry out a heat treatment suitable for decomposition of the carbides, quenching in brine. (The procedure for the heat treatment will depend on the composition of the sample.) Remove the oxide layer by filing, clean with a steel brush, and weigh the sample.

Separation of the inclusions—Carry out the electrolysis using a maximum current of 0.8 amp. and a rate of flow of anolyte of about 100 drops per minute. Check the pH of the anolyte periodically; values in the range 6.8 to 7.0 should be obtained. Stop the electrolysis after passing 20 ampere-hr. of current, the duration of electrolysis being normally about 30 hr. Remove the residue of inclusions, which will be partly on the filter of the anodic compartment and partly adhering to the undecomposed sample, and wash well with water. Dry and reweigh the undecomposed sample to determine the weight of sample corresponding to the inclusions obtained.

By this procedure obtain inclusion residues from two separate samples and treat one residue by procedure (A) and the other by procedure (B).

(A) *Determination of alumina, ferrous oxide, and combined manganous oxide*—Add 0.45 ml. of diluted hydrochloric acid (2 + 3) to 50 ml. of cupric bromide solution (200 g. in 300 ml. of water). Transfer the inclusion residue and 30 ml. of the acidified cupric bromide solution to a vessel fitted with a steam jacket. Pass into the solution oxygen-free nitrogen, begin the steam heating, and continue for 5 min. after the steam passes through the jacket uncondensed. Remove the solution and repeat the procedure for 2 min. with a further 15 ml. of acidified cupric bromide solution. Filter off the residue, washing with water, then with 10 per cent. sodium carbonate solution, and finally with water.

Ignite the residue in platinum and fuse with 6 g. of sodium carbonate. Extract the cake with water, add 1 drop of alcohol, boil and filter, washing with water. Retain the residue for the determination of ferrous oxide and combined manganous oxide.

Carefully neutralise the filtrate with diluted hydrochloric acid (2 + 3), warm to remove carbon dioxide, and dilute to 100 ml. Prepare a blank solution by fusing 6 g. of sodium carbonate, dissolving in water and neutralising with diluted hydrochloric acid (2 + 3). To compensate for any colour due to chromate in the test solution, measure the absorption of the test solution in a 5-cm. cell at 430 m μ ., with the mercury lamp, using water as a reference solution. Add the corresponding quantity of potassium chromate to the blank solution and dilute to 100 ml.

For the aluminium determination take 10 ml. of the test solution, dilute to about 30 ml., and make just alkaline to phenolphthalein with 5 per cent. sodium hydroxide solution. Carefully neutralise with 1.37 *N* hydrochloric acid (53 ml. of hydrochloric acid diluted with 450 ml. of water), adding 10 drops in excess. Add 10 ml. of 0.15 per cent. erio-chromocyanin solution (prepared 3 to 12 hr. previously) and 20 ml. of acetate buffer solution (274 g. of ammonium acetate, 109 g. of sodium acetate, and 6 ml. of acetic acid per litre), and dilute to 100 ml. After 15 min., measure the absorption of the solution in a 0.5-cm. cell at 530 m μ . with the tungsten lamp, using as a reference solution 10 ml. of the blank solution similarly treated. Calculate the alumina content of the sample from a calibration curve prepared, using standard aluminium solutions.

Dissolve the residue obtained after water extraction of the sodium carbonate melt in 15 ml. of hot, diluted sulphuric acid (1 + 3) and a few drops of hydrogen peroxide, add 10 ml. of diluted nitric acid (1 + 4), and boil. Dilute, add 10 ml. of 0.85 per cent. silver nitrate solution and 10 ml. of 50 per cent. ammonium persulphate solution and heat to 60° C. After oxidation, cool and dilute to 100 ml. Measure the absorption of the solution in a 2-cm. cell at 530 m μ . with the tungsten lamp, using water as a reference solution. The manganese figure, calculated from a calibration curve prepared, using standard manganese solutions, represents the percentage of chemically combined manganous oxide in the sample.

For the ferrous oxide determination take as much as possible of the solution used for the manganese determination, add an excess of aqueous ammonia, and boil. Filter, wash with hot water, and dissolve the precipitate in 10 ml. of diluted hydrochloric acid (1 : 1). Add a few drops of hydrogen peroxide and evaporate to 2 ml. Dilute to about 80 ml., add 1 ml. of 40 per cent. potassium thiocyanate solution, and dilute to 100 ml. Measure the absorption of the solution in a 1-cm. cell at 470 m μ . with the tungsten lamp, using water as a reference solution. Calculate the ferrous oxide content of the sample from a calibration curve prepared by means of standard iron solutions.

(B) *Determination of silica and free manganous oxide*—Extract the inclusion residue with 30 ml. of glycine solution (5 g. of glycine in 30 ml. of water), filter, and evaporate the filtrate, which contains the free manganous oxide, to dryness. Ignite, fuse with potassium hydrogen sulphate, and extract with diluted sulphuric acid (1 + 2). Determine the manganese by the procedure as in (A). The manganese figure obtained represents the free manganous oxide in the sample and must be added to the amount found by procedure (A) (combined manganous oxide) to give the total manganous oxide in the sample.

To determine silica, wash the residue from the glycine extraction with water and digest with 20 ml. of hot, diluted hydrochloric acid (1 + 10) to decompose sulphides. Filter, wash with water and then with 10 per cent. sodium carbonate solution until the washings give a negative test for

silica with ammonium molybdate solution and dilute hydrochloric acid. (The washing with sodium carbonate solution removes freshly precipitated silica formed by the action of hydrochloric acid on silicides present in the inclusions; silica present as such in the original sample remains undissolved.)

Ignite the residue and fuse with sodium carbonate. Transfer the cake to a platinum dish, decompose with 20 ml. of diluted hydrochloric acid (2 + 3), and evaporate to dryness. Add 50 ml. of concentrated hydrochloric acid, boil down to 20 ml., add 10 ml. of gelatin solution (0.5 g. in 100 ml. of concentrated hydrochloric acid), and allow to stand for 30 min. Dilute and filter, washing with hot water containing dilute hydrochloric acid and finally with hot water alone. Ignite the silica precipitate and weigh on a micro-balance.

H. J. CLULEY

Determination of Selenium in Steel. N. A. Tananaev and V. I. Murasheva (*J. Anal. Chem. Russ.*, 1948, 3, 3-6)—Selenium can be determined in the insoluble residue left after dissolution of steel in sulphuric acid, as only negligible traces of volatile compounds of selenium were found in the evolved gases obtained by treatment of 30-g. portions of steel with 150 ml. of diluted sulphuric acid (1 + 4).

Procedure—Dissolve 20 g. of steel in a 500-ml. conical flask by gentle heating on a sand-bath with 150 ml. of diluted sulphuric acid (1 + 4). Filter the solution through a filtering crucible without suction, wash the insoluble matter with hot water several times, then wash back the residue into the original flask, pour 50 ml. of concentrated nitric acid through the crucible, again wash the crucible with hot water, collecting the acid and washings in the flask containing the residue, and boil the solution until oxides of nitrogen are no longer evolved. Transfer the solution to a porcelain dish and evaporate it to dryness over boiling water. Dissolve the dry residue in concentrated hydrochloric acid, filter through a filtering crucible, rinsing the dish three times with hydrochloric acid, and wash the insoluble matter in the crucible with hydrochloric acid twice, and then twice with hot water. Treat the filtrate at 40° to 50° C. with 50 ml. of hydrochloric acid saturated in the cold with hydrogen sulphide, and allow to stand for 24 hr. Then filter through a filtering crucible, washing successively with hydrochloric acid, hot water, alcohol, and ether. Dry at 35° to 40° C. and finally at 105° to 110° C. to constant weight. The residue is selenium.

Alternatively, the determination can be finished volumetrically. Dissolve the selenium in concentrated nitric acid, make alkaline with aqueous ammonia solution and then acid with acetic acid, dilute to 400 ml. with water, add 3 g. of urea and 3 g. of potassium iodide, and titrate the liberated iodine after 1 to 3 min. with thiosulphate in presence of starch.

Tellurium does not interfere, as it remains in solution during the hydrogen sulphide treatment in the very acid medium used.

Steels containing from 0.03 to 0.095 per cent. of

selenium were analysed by this method and by the A.S.T.M. method. Results agreed to 0.002 per cent. (of the sample). Selenium-free steels were also dissolved and known amounts of selenious acid were added to the solutions. Recovery of selenium was satisfactory, e.g., amounts added 0.0025 g., 0.0085 g., 0.0636 g. of selenium—amounts found 0.0028 g., 0.0083 g., and 0.0632 g., respectively.

The method is considered to be as accurate as, and much simpler than, the A.S.T.M. method.

G. S. SMITH

Preparation of Standard Chromous Sulphate or Chromous Chloride Solutions of Determinate Concentration. J. J. Lingane and R. L. Pecsok (*Anal. Chem.*, 1948, 20, 425-428)—

Because the chromous ion is the most powerful reductant used as a standard solution, its preparation and storage are difficult. A solution of exactly determinate strength is prepared by reduction of a chromic salt of known purity by amalgamated zinc, the same vessel serving for the reaction and for storage.

Method—In the apparatus used the 1-litre, round-bottomed flask is one-half to two-thirds full of pure zinc amalgam. The solution is kept under pure hydrogen generated in a Kipp apparatus and passed through a U-tube containing some chromous sulphate in 0.1 N sulphuric acid in contact with amalgamated zinc to remove oxygen. The burette is easily removed for cleaning and is clamped in position, the reservoir being supported on a rubber-covered ring. Amalgamate about 1 kg. of mossy zinc (arsenic-, lead-, and iron-free) by stirring for a few minutes with a mercuric chloride solution in dilute hydrochloric acid, and then wash it with cold water. Between 600 and 700 ml. of chromium solution can then be accommodated in the flask.

To prepare 0.1000 N chromous sulphate in 0.1 N sulphuric acid, dissolve 29.431 g. of pure, dried potassium dichromate in about 500 ml. of water in a 2-litre Erlenmeyer flask and add 27.8 ml. of concentrated sulphuric acid. Through a long-stemmed funnel in the neck of the flask add slowly 75 ml. of pure 30 per cent. hydrogen peroxide solution, and heat the solution near the boiling-point until all the oxygen is evolved (about 20 min.). Cool to room temperature and dilute the solution to 2 litres in a volumetric flask. Rinse the storage flask twice with 100-ml. portions of the solution, and transfer the remainder. Close the flask and connect the hydrogen generator. Only a small amount of the gas is necessary to protect the solution from air and to replace the solution withdrawn.

If a solution that is normal with respect to sulphuric acid is required, add 50 ml. more concentrated sulphuric acid before diluting to 2 litres. Reduction of a full reservoir of solution takes a few hours if the flask is shaken occasionally, but complete disappearance of the chromic green colour is easily recognised. The solution in 0.1 N acid is stable for about 1 week, and that in N acid, for about 3 weeks.

For solutions of chromous chloride, appropriate

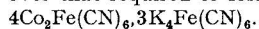
amounts of hydrochloric acid replace the sulphuric acid.

Potentiometric titration is necessary because of the green colour of chromic ion, but the end-point is sharp. A suitable titration apparatus consists of a three-necked balloon flask. An inert gas, freed from oxygen as the hydrogen was, is passed through a tube in a rubber stopper in the central neck, and a platinum-wire indicator electrode is wound round the tube. One side-neck carries a salt bridge, filled usually with 1 to 2 *N* sulphuric acid, with ends closed by internal ground-glass plugs (Irving and Smith, *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 480) for connection to a saturated calomel reference

ammonium sulphate (free from ferric ion) and titration of the resultant ferric ions gives an excellent curve, agreement again being to within ± 0.1 per cent. M. E. DALZIEL

Physico-chemical Analysis of Systems Important in Analytical Chemistry. XIII. The System $\text{CoSO}_4 - \text{K}_4\text{Fe}(\text{CN})_6 - \text{H}_2\text{O}$. I. V. Tananaev and M. I. Levina (*J. Anal. Chem. Russ.*, 1948, 3, 31-40)—Measurements of solubility and light absorption in the system $\text{CoSO}_4 - \text{K}_4\text{Fe}(\text{CN})_6 - \text{H}_2\text{O}$ have shown that the interaction between cobalt ions and potassium ferrocyanide takes place in three stages, with the formation of two double salts, $5\text{Co}_2\text{Fe}(\text{CN})_6 \cdot \text{K}_4\text{Fe}(\text{CN})_6$ and $4\text{Co}_2\text{Fe}(\text{CN})_6 \cdot 3\text{K}_4\text{Fe}(\text{CN})_6$, and solid solutions of variable composition. X-Ray spectra proved the individuality of the two double salts. From the phase diagram a method of determining cobalt was indicated.

Procedure—To 23.84 ml. of a solution of cobalt sulphate, containing 0.1320 g. of cobalt, placed in a 250-ml. graduated flask, was added from a burette 0.08320 *M* potassium ferrocyanide in quantity sufficient to coagulate the colloidal solution that formed first. The solution was then made up to the mark and shaken, and a portion of the clear liquid removed and titrated with 0.1 *N* potassium permanganate to give the excess of ferrocyanide over that required to form

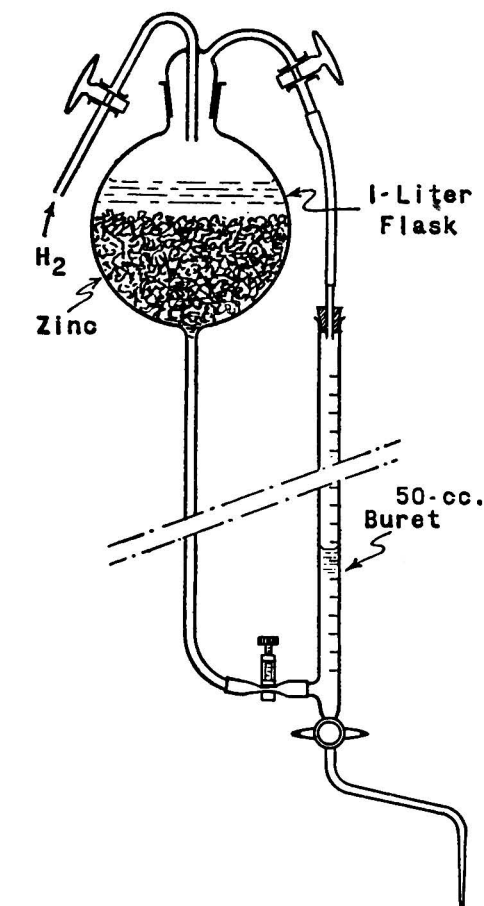


The amount of ferrocyanide solution that has to be added to cause coagulation is about double the theoretical. No adverse effect is produced by adding larger excesses of ferrocyanide.

G. S. SMITH

Analysis of Thorium - Chromium Mixtures. R. E. Ewing and C. V. Banks (*Anal. Chem.*, 1948, 20, 233-234)—Since thorium is unaffected by most oxidising agents the chromium can be oxidised and determined titrimetrically, the most satisfactory oxidising agent being perchloric acid. Any chromyl chloride evolved is condensed and titrated with the bulk solution. Thorium can be precipitated as oxalate in presence of chromium if sufficient oxalic acid is present to form the $\text{Cr}(\text{C}_2\text{O}_4)_3$ complex also, but slight contamination of the precipitate with chromium occurs. Accuracy is increased but speed forfeited if the chromium is first volatilised as chromyl chloride. The apparatus is shown.

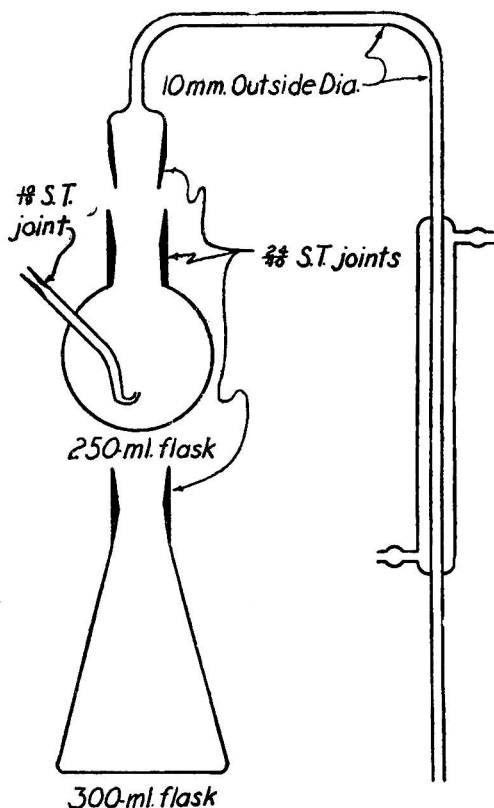
Procedure—Determination of thorium—Treat a sample containing between 200 and 300 mg. of thorium in a beaker with 10 to 15 ml. of concentrated nitric acid and 5 to 10 drops of diluted hydrofluosilicic acid (1 ml. of 48 per cent. acid + 50 ml. of water). Heat until dissolution is complete and transfer to the round-bottomed flask with 3 drops of 30 per cent. hydrogen peroxide solution and 35 ml. of 60 per cent. perchloric acid solution. Place a 300-ml. Erlenmeyer flask containing 150 ml. of water beneath the condenser so that its end is just submerged. Bubble nitrogen through the solution at a rate of 1 or 2 bubbles per second and heat the flask. When oxidation has begun



electrode through a saturated potassium chloride solution. The burette tip passes through a hole in a stopper in the third neck, slightly over-large, to allow the escape of gas. The gas stream is started 15 to 20 min. before the titration and maintained during it. When precipitates are produced, mechanical stirring is advantageous.

Standardisation against copper sulphate dissolved in diluted hydrochloric acid (1 + 1) gives results agreeing with the determinate normality to within ± 0.1 per cent. Direct titration against dichromate is erratic, but addition of a slight excess of ferrous

replace the nitrogen stream with hydrogen chloride, generated by dropping concentrated hydrochloric acid into concentrated sulphuric acid. When nearly all the chromium has been removed, transfer the solution to a beaker and concentrate it to 5 ml. to remove the excess of perchloric acid, and dilute to 300 ml. Heat to the boiling-point, and add 5 ml. of filter pulp and 5 g. of oxalic acid. Digest hot for 15 min., cool, then filter, wash, and ignite the precipitate and weigh it as ThO_2 .



Determination of chromium—Treat a sample containing between 70 and 75 mg. of chromium in a beaker with 10 to 15 ml. of concentrated nitric acid and 5 to 10 drops of hydrofluosilicic acid. When dissolution is complete, transfer to the 300-ml. Erlenmeyer flask and add 3 drops of 30 per cent. hydrogen peroxide solution and 20 to 25 ml. of 60 per cent. perchloric acid solution. The condenser dips into 150 ml. of water contained in a 200-ml. Erlenmeyer flask. Heat until oxidation is complete and cool the flask. Return the distillate to the flask and boil the solution for 20 min. to expel chlorine. Cool, and add an excess of 0.1 *N* ferrous sulphate (in 1 per cent. sulphuric acid), and titrate back with 0.1 *N* tetrasulphatoceric acid, using 1 or 2 drops of ferroin as indicator (14.8662 g. of 1 : 10-phenanthroline monohydrate and 6.9505 g. of heptahydrated ferrous sulphate in 1 litre of solution).

Results—In samples containing between 180 and 319 mg. of thorium in presence of 80 to 522 mg. of

chromium, thorium can be determined to within 0.2 mg. In samples containing between 68.5 and 75.6 mg. of chromium in presence of 42 to 210 mg. of thorium, chromium can be determined to within 0.2 mg.
M. E. DALZIEL

Thorium in Monazite Sand. Separation and Determination by Precipitation from Homogeneous Solution. H. H. Willard and L. Gordon (*Anal. Chem.*, 1948, 20, 165-169)—The main precipitation reactions employed are of the type in which the precipitant is produced uniformly throughout the sample solution by the decomposition of a suitable compound, instead of being added as a relatively localised stream of solution. The method described consists of three main parts: decomposition of monazite sand with perchloric acid, precipitation of thorium and rare earths, and separation of thorium from the rare earths. The advantages claimed over previous methods are greater speed and accuracy. Critical discussion and experimental investigations leading to the following method are given in some detail.

Decomposition of monazite sand—Weigh 50 g. into a lipped, wide-mouth, 1000-ml. conical flask, and boil vigorously with 200 ml. of perchloric acid (70 per cent.) for 1 to 1.25 hr. Do not cover the flask, as the return of water reduces the effectiveness of the acid. Cool somewhat, add 50 ml. more of perchloric acid and then, slowly and with agitation of the liquid, 300 ml. of water. Add, slowly and with vigorous shaking, 18 g. of hydrazine dihydrochloride crystals; this substance reduces and makes soluble the precipitated basic cerium phosphate. Warm gently for 1 hr. to remove gaseous decomposition products. The solid residue consists of zircon, quartz, rutile, ilmenite, and dehydrated silica. Cool the flask and add 3 g. of purified diatomaceous earth (Filter-cel). Mix thoroughly and filter through a medium grade 15-cm. paper supported by a small platinum cone. Wash the residue with diluted perchloric acid (1 + 3). Remove the paper and residue to a small beaker and macerate with a few ml. of diluted perchloric acid (1 + 3), and decant through an 11-cm. paper. Wash the residue several times, and then dilute the combined filtrates to 1 litre with diluted perchloric acid (1 + 3).

Precipitation of thorium and rare earth oxalates—To 25 ml. of the perchloric acid solution in a 600-ml. beaker add silica-free concentrated aqueous ammonia solution drop by drop, mixing thoroughly, until a permanent turbidity is produced. Add 10 ml. of concentrated hydrochloric acid and shake occasionally for 5 min. Add 100 ml. of water and 6 g. of methyl oxalate. Use slow mechanical stirring and heat the solution at 70° to 85° C. for 30 min. The oxalate dissolves, the solution becoming clear, and then hydrolyses, and precipitation of oxalates occurs. Add a hot solution of 8 g. of oxalic acid in 280 ml. of water and stir for a further 30 min., keeping the solution warm. Cool, and filter through an 11-cm., ashless paper of medium porosity, and wash the precipitate ten times by decantation with a 2 per cent. solution of oxalic

acid containing 40 ml. of concentrated hydrochloric acid per litre. Put the filter paper in the beaker containing the precipitate, add 20 ml. of concentrated nitric acid and 5 ml. of perchloric acid (70 per cent.), and warm gently until fumes of perchloric acid appear. Cool, add 200 ml. of water and 6 g. of methyl oxalate, heat and stir for 30 min. as above, add a hot solution of 8 g. of oxalic acid in 200 ml. of water, and heat and stir for 30 min. more. Cool, filter, and wash five times by decantation. Decompose the paper and oxalates by heating with 20 ml. of nitric acid and 10 ml. of perchloric acid until fumes of perchloric acid appear. The solution is then quite free from phosphate.

Separation of thorium—Cool the solution of perchlorates, and add 1 g. of potassium iodide in 25 ml. of water and then a filtered solution of 8 g. of urea, 10 g. of ammonium chloride, and 3 ml. of formic acid (90 per cent.) in 150 ml. of water. Dilute to 350 ml. and, using silica-free aqueous ammonia solution, adjust the pH to 4.45 ± 0.02 with the aid of a calibrated glass electrode. Stand a stirring rod, with a 1-mm. indentation in the lower end, in the beaker and heat so that, after bringing the solution to boiling-point, a steady stream of bubbles rises from the indentation. Boil for 95 to 97 min. after the appearance of opalescence. The final pH should be 5.4 to 6.2. If it is less than 5.4 more boiling is necessary to precipitate all the thorium. If it is above 6.2 some rare earths may precipitate, but will be removed in the second precipitation. Filter and wash ten times with a hot solution, adjusted to pH 5.6, containing 20 g. of ammonium nitrate and 8 ml. of formic acid per litre. Remove most of the thorium precipitate on the beaker walls with a "policeman." Dissolve the precipitate on the paper in hot 2 *N* hydrochloric acid and collect the solution in the precipitation beaker. Wash the paper thoroughly. Add 1 g. of potassium iodide and carry out the precipitation as described above. The final pH after 95 to 97 min. boiling should be 5.4 to 6.0. Filter and wash the precipitate ten times. Remove most of the precipitate adhering to the beaker with a "policeman" and add to the filter. Put 10 ml. of diluted hydrochloric acid (1 + 1) into the beaker, insert the stirring rod, cover, and boil very gently for 10 min. Rinse the cover glass and beaker walls, add aqueous ammonia solution drop by drop until bromocresol purple becomes purple and warm for 1 to 2 min. Filter the few milligrams of gelatinous precipitate on the filter containing the basic thorium formate and wash five times. Ignite in platinum for 2 hr. at 950° C., remove silica with hydrofluoric and sulphuric acids, and ignite for 2 hr. at 950° C. or to constant weight.

L. A. DAUNCEY

Thermal Behaviour of Analytical Precipitates. T. Duval and C. Duval (*Analyt. Chim. Acta*, 1948, 2, 97-102, 103-104, 105-109, 110-114)—**Sodium**—The precipitated chloride loses moisture below 407° C. and is then stable to 878° C. The perchlorate is precipitated as the monohydrate, but is anhydrous at 130° C., and the anhydrous salt does not decompose below 471° C.; conversion

to chloride is complete at about 620° C. The sulphate loses moisture from ordinary temperatures and becomes anhydrous between 90° and 878° C. The antimonate is precipitated with varying amounts of water, dehydration begins at 128° C., and the anhydrate is stable between 600° and 950° C. The double uranyl acetate with magnesium, $[\text{Mg}\{\text{UO}_2(\text{CH}_3\text{CO}_2)_2\}_2]\text{Na}$, is of variable composition, with between 6 and 9 molecules of water (6.5 molecules at 20° C.), but is stable to 91° C. Losses of water and acetic acid occur simultaneously and become explosive above 275° C.; the residue is $0.5 \text{ U}_2\text{O}_7\text{Na}_2 \cdot \text{U}_2\text{O}_7\text{Mg}$, is stable between 360° and 745° C., and is independent of the original precipitate. The analogous compound with zinc also contains between 6 and 9 molecules of water and is stable up to 75° C., the anhydrous range being only between 118° and 125° C. Loss of acetic acid then occurs up to 360° C. when the double pyrouranate, $0.5 \text{ U}_2\text{O}_7\text{Na} \cdot \text{U}_2\text{O}_7\text{Zn}$, which is stable below 674° C., is formed. The triple bismuth, cerium, and sodium nitrite, $6\text{NaNO}_2 \cdot 9\text{CsNO}_2 \cdot 5\text{Bi}(\text{NO}_2)_3$ is stable between 160° and 670° C.

Ammonium—The chloride is anhydrous between 40° and 126° C., but sublimation begins slowly at 110° C. Decomposition of the platinichloride, $(\text{NH}_4)_2\text{PtCl}_6$, begins at 181° C. and becomes explosive above 276° C. Between 407° and 538° C. a constant weight of platinum is obtained. The platinum is superficially oxidised to PtO at 607° C., but reverts quantitatively to platinum metal above 811° C.

Potassium—The chloride is anhydrous between 219° and 813° C. The anhydrous perchlorate is stable between 73° and 653° C., loss of oxygen occurring above that range. The pure sulphate is obtained between 408° and 880° C., no apparent sublimation occurring above 800° C. The cobaltinitrite is precipitated in a hydrated form, but there is no evidence of a stable monohydrated or anhydrous salt for use as a weighing form. Potassium per-rhenate, KReO_4 , is stable between 54° and 220° C., but decrepitation begins at that temperature. The platinichloride can be weighed below 270° C.; decomposition occurs at higher temperatures, but is not complete even at 880° C. The chloro-6-nitro-5-toluene *m*-sulphonate, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot (\text{Cl})(\text{NO}_2) \cdot \text{SO}_3\text{K}$, is stable to 278° C.; explosion occurs at 345° C. The acid tartrate is stable and anhydrous to 200° C., but chars at higher temperatures. The picrate is stable to 217° C., but explosion does not occur until 310° C. The dipicrylamine can be dried up to 220° C. without fear of explosion.

Rubidium—The anhydrous chloride is obtained between 88° and 605° C. The perchlorate is anhydrous between 95° and 343° C., decomposition beginning slowly at that temperature and becoming explosive at about 473° C. The sulphate, prepared from rubidium chloride and sulphuric acid, is dehydrated at 76° C. and is then stable to 877° C., with no apparent sublimation; when prepared from the acid carbonate no stable compound is formed even at 880° C.; this behaviour appears to be due to the formation of acid sulphates. The hydrated cobaltinitrite decomposes in complex fashion,

constant weight being attained between 283° and 550° C., but the mixture of cobalt oxide, rubidium nitrate, and sodium nitrate formed is of variable composition. The stannichloride, Rb_2SnCl_6 , is stable to 341° C. and loss of chlorine and stannic chloride occurs between 407° and 650° C., the residual mixture of rubidium chloride and stannic oxide of variable composition being stable between 650° and 812° C. The platinichloride is stable below 674° C., decomposing slowly up to 1000° C. into platinum and into rubidium chloride, which sublimes slowly.

M. E. DALZIEL

Electro-Oxidation of Quadrivalent Uranium.
R. H. Betts (*Canad. J. Res.*, 1948, 26, B, 441-455)—The effect of various factors on the current efficiency of the electrolytic oxidation of quadrivalent uranium at a platinum anode has been studied.

The apparatus consists of two 100-ml. beakers serving as anode and cathode compartments, respectively, connected by a removable U-tube. A rectangular sheet of platinum, 3.0 sq. cm. in area, which can be rotated in one of the beakers at 300 to 500 r.p.m., serves as anode. A stationary platinum cathode is used and the anode potentials are measured with reference to a saturated calomel electrode connected to the anode compartment by means of a second U-tube filled with perchloric acid. Two 6-v. batteries connected to the electrodes through a rheostat provide the current, which is measured by a milliammeter in the circuit.

Procedure for measuring current efficiencies—Pipette suitable volumes of 1.0 N perchloric acid into the two beakers, and fill the U-tube with the same acid. Adjust the applied potential to give the required current density and then add a known volume of a uranous sulphate solution in 1.0 N perchloric acid. After the oxidation has proceeded for a measured time, determine the quadrivalent uranium remaining in the anode compartment by titration with potassium permanganate.

The current efficiency increases linearly with increasing uranium concentration. It decreases rapidly at first and then more slowly with increasing current density.

J. G. WALLER

Microchemical

New Technique for the Micro-determination of Iron. **L. Deibner** (*Bull. Soc. Chim.*, 1948, 615-629M)—A detailed re-investigation of the iodimetric method has been made. In order to establish precisely the conditions found to be most satisfactory the iron is first precipitated as hydroxide and is redissolved in hydrochloric acid of definite concentration. The following factors influencing the accuracy of the method have been studied: type of filter, washing of the precipitate, concentration and volume of acid, use of carbon dioxide to eliminate dissolved oxygen, quantity of potassium iodide, and duration of the reaction. Starch mucilage (0.2 per cent.) is used as indicator and, with the very dilute solutions employed, the end-point is not a sharp change from blue to colourless, but is preceded by a succession of colours, *viz.*,

blue, purple, red, violet, rose and yellow. This phenomenon is the more pronounced the greater is the concentration of potassium iodide and, even at the concentration of iodide employed, careful observation of the end-point is necessary.

Reagents—Strong emphasis is placed on the purity of all reagents, and the water used for most of the solutions is previously boiled. (1) Potassium iodide solution containing 1 g. in 1 ml. If this solution is yellow, decolorise it with N/75 or N/150 sodium thiosulphate; if it is colourless, add a slight excess of 0.01 N iodine and decolorise with thiosulphate. (2) Potassium iodide solution, 3 per cent., prepared in the same manner. (3) N/75 Sodium thiosulphate, prepared according to Hanes (*Biochem. J.*, 1929, 23, 99) and kept in an amber glass bottle connected to the micro-burette through a syphon covered with black paper. Standardise this solution on a solution of 0.4 to 0.8 g. of potassium iodate per litre, using 3 ml. of the iodate solution, 3 ml. of 3 per cent. potassium iodide solution, and 3 ml. of 3 per cent. acetic acid. Allow this mixture to stand for 3 min., add 0.6 ml. of starch mucilage, and titrate with the thiosulphate solution.

Procedure—Use preferably a cylindrical 50-ml. vessel with a ground-glass stopper. The iron solution should be slightly acid and free from interfering elements and should contain 0.04 to 1 mg. of Fe as ferric chloride in 20 ml., the volume taken for analysis. Add 2 to 2.5 ml. of diluted hydrochloric acid (1 + 2), a few drops of hydrogen peroxide (110 volumes) and two glass balls, cover with a watch-glass, and boil for 1 min. Add about 0.5 g. of ammonium chloride or sulphate and a large excess of concentrated aqueous ammonia solution, keep at 50° to 60° C. for 30 to 45 min., then allow to stand for 2 to 3 hr. Separate the ferric hydroxide by means of a sintered-glass immersion filter, porosity 4, immersing the filter to the minimum extent. Connect the filter to the pump through a filter flask and fit a stopcock on a T-tube to allow regulation of the reduced pressure. Wash the vessel and filter with 150 to 200 ml. of 0.5 per cent. ammonium chloride or sulphate solution at 70° to 80° C. and then with about 75 ml. of hot water. Remove the water from inside the filter with a rubber-tipped capillary tube connected to the pump and dry the filter by aspiration without removing it from the precipitating vessel. Measure into the vessel 10 ml. of dilute hydrochloric acid (4 g. per litre) and warm it. Connect a tube containing a plug of cotton wool to the end of the filter and suck the warm acid through the filter-plate several times. Then connect the tube to a small pump and eject the liquid into the vessel. Use 5 ml. more of the dilute acid to wash the outside of the filter and to wash the plate twice from the inside, introducing it through the tube and ejecting it through the plate. From this point conduct a parallel blank experiment starting with 15 ml. of dilute hydrochloric acid (4 g. per litre). Pass through the liquid for 5 min. a current of pure carbon dioxide. Raise the gas delivery tube above the liquid surface without interrupting the gas current, add 1 ml. of

potassium iodide solution (1 g. per ml.), mix, stopper, and allow to stand for exactly 5 min. Titrate with *N*/75 or *N*/150 sodium thiosulphate from a 2-ml. micro-burette adding 0.8 ml. of starch mucilage when the colour becomes pale yellow. Stir the solution after each addition, and towards the end of the titration add the thiosulphate in quantities of 0.005 ml. at intervals of several seconds. The end-point (*vide supra*) is best observed against a piece of opal glass and it should be checked after a final interval of 30 to 40 sec.

Results of a large number of determinations show errors varying between -5.6 and $+7.8$ per cent.

W. C. JOHNSON

Physical Methods, Apparatus, etc.

Crystallographic Data, Armour Research Foundation of the Illinois Institute of Technology (*Anal. Chem.*, 1948, 20, 491-492)—The crystallography of ethylenediamine *D*-tartrate and hemihydrated dipotassium hydrogen tartrate is set out under the headings listed in the first publication of the series (*Ibid.*, 1948, 20, 275; *Abstr.*, *Analyst*, 1948, 73, 579).

M. E. DALZIEL

Crystallographic Data, Armour Research Foundation of the Illinois Institute of Technology (*Anal. Chem.*, 1948, 20, 593-595)—Data are given for *p*-methyl aminophenol sulphate (Metol, Elon) and *p*-aminoazobenzene (Aniline Yellow S) under the headings listed in the first paper of the series (*cf.* preceding abstract).

M. E. DALZIEL

Accelerated Method for Measuring the Penetration of Water in Insulation Board. W. A. Wink and J. A. Van den Akker (*Paper Trade J.*, 1948, 127, Sept., *T.A.P.P.I. Sect.*, 371-376)—Grant's method (*Analyst*, 1935, 60, 60) for rendering water penetration through paper visible by use of a fluorescent indicator, is extended to boards.

Procedure—Cut a disc of sample (minimum diameter 6 in.), seal the edges with wax, and place it horizontally on water at $130 \pm 0.5^\circ \text{F.}$, so that the lower surface is immersed to a depth of $\frac{1}{4}$ in. After a period appropriate to the nature of the sample (1 to 2 hr.), saw the specimen into four quarters, at once sprinkle the cut edges with powdered Uranine-B (using a pepper-box, covered with an 80- to 100-mesh wire), and examine them in filtered ultra-violet light. The light yellow fluorescence of the damp dye shows the depth to which penetration has occurred, and enables it to be measured with an accuracy to $1/16$ in. Experimental data are tabulated, and are in agreement with values obtained from direct measurements of the distribution of the water in the board.

J. GRANT

Spectrographic Determination of Sodium in a Silica-Alumina Catalyst. J. B. Marling (*Anal. Chem.*, 1948, 20, 299-300)—Sodium is determined in a silica-alumina catalyst by a simple and rapid spectrographic method. The sample is

placed in the crater of a graphite electrode and is excited by a 2300-volt, 2.5-amp., A.C. arc. The counter electrode is of high purity copper, and copper lines are employed as internal standards. Each sample is analysed three or four times and the results are averaged, giving a final result sufficiently accurate for industrial control and more accurate than the average chemical method for low percentage ranges. The time taken for an analysis is 30 to 50 min. The method has been tested by comparison with chemical analyses and the average deviation in the specification range (0.02 per cent. of Na_2O or less) is 0.002 per cent. of sodium oxide.

Modifications to the technique employed are suggested as a means of improving its accuracy, but have not been checked experimentally.

H. R. CLAYTON

Emission Spectroscopy in an Oil Laboratory.

R. G. Russell (*Anal. Chem.*, 1948, 20, 296-298)—The applications of emission spectrographic analysis in an oil laboratory are described. For general qualitative work the D.C. arc is used and the samples, in the form of oils, liquids or organic residues, are either evaporated to dryness or ignited and burned. The resulting material is mixed with graphite powder and loaded into a cavity in the end of a graphite or copper rod that is then arced. For qualitative analysis of surface films a series of low-powered, short-duration, alternating-current spark discharges is employed with a graphite rod as counter electrode. The limit of detection by this method is 0.000001 g. of material. As an example of quantitative methods the analysis of silica-alumina catalysts is described (*cf.* preceding abstract). Standard samples are prepared by addition of known amounts of sodium chloride to samples of a catalyst that is substantially free from sodium and these standard samples are included on each analytical plate. The standards and samples are prepared for analysis by mixing 1 g. of the material with 2.2 g. of pure graphite powder and 50 mg. of lithium carbonate, which is used as an internal standard. The resultant powder is briquetted and used as the lower electrode of an alternating-current spark discharge. The upper electrode is a graphite rod of $\frac{1}{4}$ -in. diameter, with a hemispherical conical tip. Four analyses are made of each sample and the average of these results is more accurate than the routine chemical determinations. The analysis of brines, a method of analysis of oil additives, and a technique for dealing with small quantities of solutions, are briefly mentioned.

H. R. CLAYTON

Study of Reversibility of Processes at the Dropping Mercury Electrode by Changing Discontinuously the Polarising Voltage.

M. Kalousek (*Coll. Czech. Chem. Comm.*, 1948, 13, 105-115)—The reversibility of a polarographic reaction can be investigated by continually altering the potential applied to the cell. A simple electric circuit is described by which the potential of the

dropping mercury electrode can be alternated five times per sec. between two potentials that are from 60 to 400 mv. apart. At the same time, the potential of the electrode is gradually increased as in normal polarographic procedure. If the electrode reaction is a reversible reduction, an

anodic current is obtained when reduction occurs at the more negative potential and not at the less negative. If the reduction is irreversible, only the cathodic current is obtained. Analogous phenomena are exhibited by oxidation reactions.

J. G. WALLER

Reviews

BRITISH CHEMICAL NOMENCLATURE. By A. D. MITCHELL, D.Sc., F.R.I.C. Pp. viii + 156. London: Edward Arnold & Co. 1948. Price 21s.

Chemical nomenclature is not one of the most popular of pastimes, at all events in this country, but there are signs that the general apathy of chemists to the subject is disappearing; witness the fact that one of the largest lecture theatres in London could barely accommodate the audience that assembled to hear Dr. G. M. Dyson lecture on his new system of notation. It is to be hoped that Dr. Mitchell's book will meet with the same degree of interest; for the conventional method of describing chemical substances, which forms its subject, will be in use for a long time to come, even though some system of notation is used for indexing, and the official adoption of any system will be useless unless individual chemists take the trouble to learn the rules and then apply them intelligently. With the publication of "*British Chemical Nomenclature*," there is no longer the excuse that it is impossible to find out what the rules are.

Even the most inexperienced of chemists, when looking up references to a particular compound that can be described quite correctly in several different ways, must appreciate how much time can be saved if he knows, for example, the order in which the substituents should be listed or the recognised name of the fundamental ring system from which the substance is derived. It is perhaps not so well known, that in spite of the efforts of the International Union of Chemistry, considerable discrepancies still exist in the methods adopted in different countries in the naming and numbering of ring systems, for instance. Dr. Mitchell deals with these and many other difficulties, some of which are too often dismissed as worthless trifles. Do we, for example, use Greek and Latin numerical prefixes correctly? Do we know when to use "primed" numbers? How many ways are there of misusing that over-worked prefix "bi"? When is "naphtho-" correct and "naphtha-" incorrect? Should the well-known plant hormone be called indoleacetic acid or indolyacetic acid? Here, indeed, is a wealth of material for a chemical "quiz"!

Not that Dr. Mitchell solves all these problems for us, for as he says in the preface: "It is impossible to lay down rules to cover even all the simpler compounds, and it is necessary to allow considerable latitude in the use of trivial names, but this volume aims at a statement of conventions adopted in the *Journal of the Chemical Society*. The view taken by successive editors of that journal has usually been that, nomenclature being such a complex subject, a name that is free from any possibility of ambiguous interpretation is the primary requisite, and if two or more names fulfil this condition they may be equally acceptable provided they do not infringe any usages." He does, in fact, achieve a very nice balance between the rigidity necessary to prevent chaos and the flexibility that is a pre-requisite to international (and sometimes intranational) agreement.

Part I of "*British Chemical Nomenclature*" is an account of the general principles of nomenclature, and Part II describes their application to inorganic chemistry. This second part is largely an exposition of the rules adopted by the International Union of Chemistry, and some of the conclusions reached are revolutionary. Henceforth, for example, sodium hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$) must be called sodium dithionite, and potassium metabisulphite ($\text{K}_2\text{S}_2\text{O}_5$) potassium pyrosulphite. But the biggest shock of all is provided by the statement that the name "sodium bicarbonate" is no longer permissible and should be replaced by "sodium hydrogen carbonate." The sections on co-ordination compounds and complex salts (borates, silicates, tungstates, etc.) make less startling innovations and the systems proposed are both simple and logical—qualities that do not always go together.

Part III, forming three-quarters of the book, deals with organic chemical nomenclature, and recounts the difficulties introduced by the adoption of different systems or by the absence of any system, and the attempts made to resolve these difficulties by Richter, Stelzner, the Ring Index, *Chemical Abstracts* and the International Union of Chemistry. The author shows great skill in piloting his readers through these very troubled waters, and all chemists engaged in the preparation of new substances should make themselves thoroughly familiar with the relevant sections of this book before presuming to name any new compound. They will thereby avoid the grievous sin of burdening the literature with incorrect names, which are almost impossible to eradicate once they have come into general use. It is valuable to have the various conventions available in such a convenient form with the benefit of Dr. Mitchell's expert comments. The book is up-to-date, and includes the rules recently proposed for indicating the orientation of sugars and amino acids and a description of that most useful device, the "oxa-aza convention."

Apart from its value to chemists actively engaged in the synthesis of new compounds, and to those responsible for editing scientific papers and reports, "*British Chemical Nomenclature*" will be found useful by the general chemist for purposes of reference. It has obviously been most carefully edited, no easy matter in view of the number of graphic formulae that it contains, and is well indexed. The excellent binding also deserves a word of praise.

F. A. ROBINSON

SPECTROSCOPY AND COMBUSTION THEORY. By A. G. Gaydon, D.Sc. Second Edition. Pp. xii + 242. London: Chapman & Hall, Ltd. 1948. Price 25s.

The mechanisms of the various combustion phenomena are still imperfectly understood both from the physical and from the chemical standpoint. The theories advanced in this field are necessarily based on evidence that is not always direct and the interpretation of which is therefore often largely conjectural. Progress is to a certain extent restricted by the lack of observations, a fact that is not surprising in view of the wide range of the subject, and its comparative infancy. Information is now, however, being rapidly gathered, and a growing number of communications are appearing in the literature on various aspects of combustion. This second edition of Dr. Gaydon's book, published six years after the first, is therefore appropriate and welcome.

The opening chapter, which introduces the reader to an outline of molecular spectra, remains unchanged. This is to be regretted, as the treatment is of necessity so brief that it seems insufficient to enable the non-specialist to appreciate much of the theoretical development which follows. After a further general consideration of the appearance and the interpretation of various spectra, and an expanded survey of the experimental problems, there follow chapters devoted to various flames. The flames considered are those of hydrogen, the hydrocarbons, carbon monoxide, inorganic elements and compounds, cool and atomic flames and explosions. For each of these, details are given of the appearance of the spectra and an assessment is made of the significance of the various systems observed. The four plates which illustrate the features discussed in these and later chapters reproduce nineteen spectra, in place of the original ten, and are better laid out, with the accompanying descriptions on the opposite pages.

The ninth chapter, a new one, is concerned with continuous spectra and the rôle of atomic oxygen in flames, the presence of which can be demonstrated by the appearance of a yellow-green continuum on addition of a small amount of nitric oxide to the flame gases. Dr. Gaydon has applied this test to several flames and discusses the bearing of the results on proposed combustion mechanisms.

The subsequent chapters make several approaches to the general subject: absorption spectra with special reference to slow burning and the internal combustion engine, the infra-red region with its practical difficulties, life-times of activated molecules and the author's theory of after-burning, the measurement and calculation of flame temperatures and dissociation energies. Many of these ideas are interwoven and demonstrate well the many ways in which reactions in flames are being investigated. Finally, under the heading "Kinetic Spectroscopy," Dr. Gaydon indicates lines of study which he believes will prove most fruitful in analysing flame reactions by the spectroscope. As with general chemistry, the original observations were largely qualitative, but now more quantitative data are required in all regions of the spectrum.

There are six appendixes containing much useful information on absorption and emission spectra and atomic and molecular energy levels and also a bibliography comprising 301 references. The book is printed on better paper than the original war-time edition, and revision and expansion of the text have enlarged it by about fifty pages. In all, it is a readable book which fills a gap, and fills it well.

ROLAND A. FINCH

APPLIED CHEMISTRY: A PRACTICAL HANDBOOK FOR STUDENTS OF HOUSEHOLD SCIENCE AND PUBLIC HEALTH. By C. KENNETH TINKLER and HELEN MASTERS. Second Edition, revised and reprinted. Vol. II: FOODS. Pp. x + 284. London: The Technical Press Ltd. 1948. Price 16s. net.

This book, with its companion first volume, is intended primarily for students taking the course in Applied Chemistry for the degree of B.Sc. (Household and Social Science) of the University of London. Its scope is indicated by its chapter division—Milk; Edible Oils and Fats; Carbohydrate Foods; Raising Agents; Meat and Meat Extracts; Vinegar, Fruit Juices and Vegetable Acids; Beverages; Preservation of Food; Poisonous Metals in Foods; Cooking of Food; Condiments; Calorific Value of Foods.

The text is largely concerned with the examination and analysis of foods, and the methods described are mainly those in routine use in a public analyst's or food manufacturer's laboratory. Objection must be raised to the inadequate treatment accorded to the determination of the freezing-point of milk by means of the Hortvet cryoscope. Although references to reports of the work of Elsdon and Stubbs in *The Analyst* are given, a method so important as this is worthy of fuller description, even in an elementary textbook. The experimental details are omitted, there is no indication of the range of the freezing-point of normal milk, there is a suggestion, perhaps unintentional, that the Hortvet cryoscope and the Beckmann cryoscope are interchangeable, and the statement that supercooling must be avoided is surprising when the principle of the Hortvet apparatus is the attaining of a definite and reproducible degree of supercooling before freezing.

Where necessary the theoretical bases of the methods are lucidly explained and the student will acquire a good knowledge of routine food analysis, but he is not always provided with the correct means of interpreting his results, especially if he is interested in the legal aspect of food examination. He is not informed that the legal standard for milk is a presumptive one, and there is a suggestion on page 168 that the inclusion of cereal filler in sausages is adulteration. The statement that preservatives are not allowed in butter and margarine requires qualification, since margarine manufactured under Government licence now contains boron preservative. Again, starch added to mustard is not necessarily an adulterant.

Admittedly it is impossible in a book of this kind to guide the student through the mass of variable and transient war-time and post-war-time legislation affecting food composition, but mention might have been made of the standards established by the Ministry of Food for such materials as Baking Powder (otherwise afforded very full treatment in the book), Mustard, Self-Raising Flour and Preserves, especially since some of the Statutory Rules and Orders establishing these standards describe the method by which the food is to be examined.

In the section on pasteurised milk the test with *p*-phenylenediamine for the destruction of peroxidases is described, but there is no mention of the more recent and more important test for adequate pasteurisation depending upon destruction of the phosphatase by heat.

In spite of these deficiencies the book can be recommended as a comprehensive practical introductory course for the student of the application of chemistry to the examination of food, especially if he consults the original papers cited in the text, and supplements his reading with a leisurely browsing through Bell's "*Sale of Food and Drugs*," a book included in the bibliography at the end of the volume.

Type and paper are good and the binding is firm and attractive. Of the few typographical errors the only one needing mention is the appearance of 10° (degrees) for 10⁰ (10 to the power of nought) on page 185.

A. O. JONES

ORGANIC ANALYTICAL REAGENTS. By F. J. WELCHER, Ph.D. Vol. III, pp. xi + 593. Vol. IV, pp. xiii + 624. New York: D. Van Nostrand Company Inc. London: Macmillan & Co. Ltd. 1947 (Vol. III), 1948 (Vol. IV). Price, each volume, 44s. net.

The plan of this work has already been described in the detailed review of the first two volumes (*Analyst*, 1948, 73, 420). The third volume, unlike the others, is divided into three parts, namely, Heterocyclic Nitrogen Compounds, the Oximes and Acidic Imino Compounds. The book begins with a chapter on pyridine and its derivatives, and the analytical utility of the parent substance, as well as the thoroughness of the presentation, is strikingly illustrated by the 43 pages of subject-matter and the list of 170 references. Also included in this first part is an important chapter on dipyrityl and related compounds. The second part begins with a discourse on the analytical applications of the dioximes, and herein one finds a monograph concerning the use of dimethylglyoxime in which 303 references are cited. This section of the book also includes, among others, chapters on *isonitroso* compounds, nitroso phenols, miscellaneous oximes and cupferron. The high light of the third part is the exhaustive study, both theoretical and practical, of diphenylthiocarbazone, in which 212 references are recorded. Many data have been published about the conditions under which metallic complexes of this reagent are formed and many procedures for attaining various degrees of specificity have been proposed. The mass of original literature devoted to this theme is indeed a tortuous maze, and the well-arranged account presented will certainly prove to be of great value.

Perhaps the most important substance discussed in Vol. IV is sodium diethyldithiocarbamate, which is one of six reagents assembled in a chapter devoted to the dithiocarbamates. While all the essentials of its use are given, together with 69 references, the transcription of the procedure due to L. A. Haddock and N. Evers (*Analyst*, 1932, 57, 495) might advantageously have included the useful table of colour values in terms of Lovibond units, given in the original paper. As with the previous volumes, some of the monographs hardly seem to warrant their allotted space; for example, the one on sodium tauroglycocholate for which the only recommended use is its addition to reaction mixtures of 8-hydroxyquinoline and magnesium salts to prevent the precipitate from adhering to the sides of the beaker. However, it is more important to mention that the text concludes with 267 pages of invaluable information concerning the application of dyestuffs to analytical chemistry.

Summarising, it is the considered judgment of the reviewer that these two volumes, like their predecessors, ought to be added to every chemical library throughout the world.

N. L. ALLPORT

Notice

MICROCHEMISTRY GROUP

MEETING IN BELFAST, MAY 10TH-11TH, 1949

A MEETING of the Microchemistry Group, jointly with the Belfast and District Sections of the Royal Institute of Chemistry, the Chemical Society and the Society of Chemical Industry will be held on the above dates.

On the afternoon of Tuesday, May 10th, there will be a tour of the Biochemistry, Chemistry and Agricultural Chemistry Departments of the Queen's University, Belfast. This will be followed by a meeting in the evening at the University, at which the following papers will be read.

"Some Microchemical Problems Associated with Plant and Animal Nutrition," by Stewart McConaghy, B.Sc., M.Agr., A.R.I.C., Dept. of Agricultural Chemistry, Queen's University of Belfast.

"The Micro-Determination of Oxygen in Organic Compounds by Reduction with Carbon," by W. T. Chambers, B.Sc., Ph.D., A.R.I.C., of The British Rubber Producers' Research Association, Welwyn Garden City, Herts.

On Wednesday, May 11th, there will be a coach tour of the famous Antrim Coast Road.

ADDRESS OF THE HONORARY SECRETARY OF THE GROUP

From now on, the address of the Hon. Secretary of the Microchemistry Group, Mr. Donald F. Phillips, A.R.I.C., is 10, Richmond Road, Blackpool, N.S., Lancs.

Metropolitan Borough of Southwark Appointment of Assistant Analyst

APPLICATIONS are invited for the appointment of Assistant Analyst in the Public Analyst's Department at a salary in accordance with Grade APT III of the National Joint Council scale, i.e. £480 rising to £525 per annum (£10 less if under 28 years of age).

Applicants should hold a University degree or an equivalent diploma in Chemistry or the Associateship of the Royal Institute of Chemistry. Some experience in the analysis of food and drugs would be an advantage.

The appointment will be subject to the Council's Conditions of Service, to the provisions of the Shoreditch and Other Metropolitan Borough Councils (Superannuation) Acts, 1922-1937, to the passing of a medical examination and to one month's notice on either side.

The Council is not in a position to assist in the provision of housing accommodation.

Applications should be made on forms obtainable from me and returned not later than a fortnight after the appearance of this advertisement.

Canvassing in any form will disqualify.

D. T. GRIFFITHS,
Town Clerk.

Town Hall,
Walworth Road, S.E.17.
1st April, 1949.

CITY OF LEEDS PUBLIC HEALTH DEPARTMENT

ASSISTANT ANALYST required in the City Analyst's Laboratory. Applicants should possess either a University degree or the Associateship of the Royal Institute of Chemistry, and preferably have had some experience in the analysis of food and drugs.

The commencing consolidated salary will be in accordance with Grade APT II of the National Scheme of Conditions of Service, commencing at £420 per annum, with increments of £15, subject to satisfactory service to a maximum of £465.

Applications, on a form to be obtained from the undersigned, giving details of age, qualifications and experience, together with the names of three referees and endorsed "Assistant Analyst," to be delivered without delay at the Health Department, 12, Market Buildings, Leeds, 1.

Canvassing in any form, either directly or indirectly, will be a disqualification.

I. G. DAVIES,
Medical Officer of Health,
School Medical Officer.

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Continued on next page

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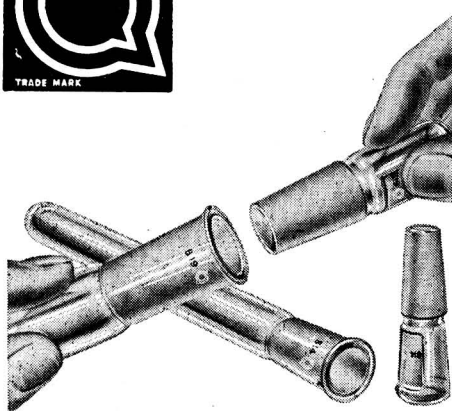
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