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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 7th. The President, Mr. F. W. F. Arnaud, took the chair for the first part of the meeting, his place being subsequently taken by Mr. John Evans, Vice-President.

Certificates were read in favour of Clifford Kenneth Boundy, A.I.C., Raphael Heber Callow, M.Sc., A.I.C., Miles Ernest Catt-Camfield, John Dewar, B.Sc., Clifford Walter Herd, B.Sc., Ph.D., F.I.C., Henry Humphreys Jones, F.I.C., and Frederick Leigh Okell, F.I.C.

The following were elected Members of the Society:—Ernest Edward Unwin Abraham, B.Sc., F.I.C., Enid A. M. Bradford, B.Sc., Frank Brookhouse, B.Sc., A.I.C., Gerald Harry Edwards, B.Sc., A.I.C., Jack Firth, A.I.C., Albert E. Fletcher, F.I.C., Patrick Sarsfield MacMahon, M.Sc., F.I.C., Moses Puffeles, Edgar Alexander Raynor, B.Sc., A.I.C., Bernard Joseph Styles, Viscount Tiverton, Cecil Edgar Wiseman, B.Sc., A.I.C., A.C.G.F.C.

The following papers were read and discussed:—"Further Notes on the Identification of Woods and Charcoals," by J. Cecil Maby, B.Sc.; "The Characteristics of Millet Oil," by Winifred E. Smith, B.Sc., A.I.C., and Edith K. Waller, B.Sc. (*Work done under the Society's Analytical Investigation Scheme*); "The Stability of Vitamin *A* in Cod-liver Oil Emulsions," by H. N. Griffiths, B.Sc., T. P. Hilditch, D.Sc., F.I.C., and J. Rae; "The Validity of the Lovibond Tintometer Method in the Assay of Vitamin *A*," by E. Lester Smith, M.Sc., A.I.C.; and "Some Properties of Ergosterol and Calciferol," by A. L. Bacharach, B.A., F.I.C., E. Lester Smith, M.Sc., A.I.C., and S. G. Stevenson, B.Sc., B.Pharm., F.I.C.

NORTH OF ENGLAND SECTION

A MEETING of the Section was held in Sheffield on December 3rd. The Chairman (Mr. J. Evans) presided over an attendance of thirty-nine. Prof. W. H. Roberts gave a brief account of the career of the late A. Chaston Chapman, F.R.S., F.I.C., and an appreciation of his life and work.

The following papers were read and discussed:—"The Estimation of the Sizes of Particles in Chocolate," by H. M. Mason, M.Sc., F.I.C., and "A Note on the

Composition of some Fatty Material found in Ancient Egyptian Tombs," by A. Banks, Ph.D., and T. P. Hilditch, D.Sc., F.I.C.

Reminiscences of the days spent in the laboratory of A. H. Allen were contributed by Messrs. J. Evans, A. R. Tankard, and S. E. Melling. Some interesting exhibits were shown, including a photograph of Dr. James Allan, the predecessor of A. H. Allen, and also the original manuscript of Volume I of the first edition of *Allen's Commercial Organic Analysis.*

A Colorimetric Method for the Determination of Chloroform

By W. G. MOFFITT, Ph.D., A.I.C.

(*Read at the Meeting, October* 5, 1932)

The colour reaction described by Lustgarten (*Monatsh. Chem.*, 1882, **3**, 715) between chloroform and α- or β-naphthol in strong potassium hydroxide solution lends itself to the rapid colorimetric determination of chloroform.

The method, whilst of limited accuracy, can be used with advantage where methods based upon the action of alcoholic potash on chloroform break down owing to the presence of other readily decomposed chloro-compounds.

When this reaction is used for the detection of chloroform, Lustgarten recommended that it should be carried out at a temperature of 50° C., when it gives rise to an intense Prussian blue colour. For comparative work it is better to allow the reaction to proceed at room temperature, when the colours are found to be of satisfactory depth and, with 0·001 to 0·003 ml. of pure chloroform, to form a well-graded series, increasing in intensity with the concentration of the chloroform. The utility of the method is determined chiefly by the strength of the potassium hydroxide solution. This controls the sensitivity of the reaction, the rate at which the colours fade, and, in part, the value of the reaction as a specific test for chloroform.

The reaction has been studied with both α- and β-naphthol; although the former appears to be the more sensitive reagent, β-naphthol gives better colours and is less liable to interference by other compounds.

Solutions Required—1. 2·0 grms. of β-naphthol dissolved in 100 ml. of 40 per cent. cold potassium hydroxide solution.

2. A standard solution (0·5 per cent. by volume) of chloroform dissolved in industrial methylated spirit (95 per cent. of ethyl alcohol).

Procedure—Ten ml. of the β-naphthol solution are measured into each of several Nessler glasses; measured volumes of the standard chloroform solution are then added to each tube, and sufficient industrial methylated spirit to make the total volume 11·0 ml. (In practice, the methylated spirit is added before the chloroform, and both are delivered with the tip of the pipette dipping slightly

below the surface of the liquid.) The tubes are then shaken and allowed to stand for 5 to 10 minutes.

Example.

Number of tube:	1.	2.	3.	4.	5.
Naphthol solution, ml.	10·0	10·0	10·0	10·0	10·0
Industrial methylated spirit, ml.	0·8	0·7	0·6	0·5	0·4
Chloroform (0·5 per cent. solution), ml. ..	0·2	0·3	0·4	0·5	0·6
Colour intensities as ratios	1·8 :	3·0 :	4·0 :	5·0 :	6·2

The ratios of the colour intensities were measured by means of a Duboscq colorimeter.

Experiments were carried out to determine how far other chloro-compounds interfered with the method. The following compounds were studied:—Methylene chloride (b.pt., 41·6° C.); acetylene dichloride (b.pt., 55° C.); ethylidene chloride (b.pt., 59·9° C.); carbon tetrachloride (b.pt., 76·7° C.); ethylene chloride (b.pt., 83·7° C.); trichloroethylene (b.pt., 87·1° C.); dichloroethyl ether (sym.) (b.pt., 178° C.).

With carbon tetrachloride a blue colour was obtained with α-naphthol; this colour was intensified by the presence of acetone. No colour was obtained with β-naphthol and any of these compounds. Acetone was found to have no interfering effect when β-naphthol was used.

Slight variations were observed in the chloroform tubes when some of the above compounds were present in large excess, but these variations were observed with β-naphthol only after the solutions had been standing for more than ten minutes.

ANALYSES OF FRESHLY-PREPARED MIXTURES

No.	Composition (by vol.)	Per Cent.	Chloroform (by vol.) found Per Cent.
1.	Chloroform	8·0	8·0
	Industrial methylated spirit	92·0	
2.	Chloroform	5·4	5·4
	Industrial methylated spirit	94·6	
3.	Chloroform	3·3	(i) 3·4 (ii) 3·5
	Methylene chloride	6·6	
	Acetylene dichloride	3·3	
	Industrial methylated spirit	86·8	
4.	Chloroform	8·3	8·3
	Methylene chloride	20·0	
	Carbon tetrachloride	20·0	
	Industrial methylated spirit	51·7	
5.	Chloroform	12·5	(i) 12·2 (ii) 12·8
	Lin. belladonnae	87·5	
6.	Chloroform	20·0	19·7
	Lin. belladonnae	40·0	
	Lin. aconiti	40·0	

A small volume (usually 3 to 5 ml.) of the sample under examination should first be distilled with 75 ml. of methylated spirit. At least 50 ml. of distillate should be collected to ensure the distillation of all the chloroform.

The distillate should then be treated in the manner described above, and the colours compared with those obtained with the standard solutions of chloroform treated at the same time. (It is essential that comparison be made within a few minutes.)

SUMMARY—Conditions are given for the colorimetric determination of chloroform by means of β-naphthol in strong potassium hydroxide solution.

None of seven chloro-compounds was found to have an appreciable influence on the reaction.

I am indebted to the Government Chemist for permission to publish this note, and to Mr. G. F. Sheppard for advice.

THE GOVERNMENT LABORATORY,
LONDON, W.C.2

The Determination of Benzoyl Peroxide in Flour

BY JOHN RALPH NICHOLLS, B.Sc., F.I.C.

BENZOYL peroxide is sometimes used for bleaching flour, and the usual methods for its detection depend upon the oxidising action of the unchanged peroxide. In effecting its bleaching action the peroxide is reduced to benzoic acid and, if the whole of the added peroxide is so changed, none remains to give an indication that the flour has been treated. A method which would determine the residual benzoic acid would serve this purpose.

The proportion of benzoyl peroxide which is used is about 1 part to 50,000 parts of flour. In order to be able to test reasonable quantities of flour, say 50 grms., it is necessary to be able to detect and to determine amounts of benzoic acid of the order of a milligram.

I have described a method (ANALYST, 1928, **53**, 19) for determining small quantities of benzoic acid, depending upon its controlled oxidation to salicylic acid and the determination of the latter colorimetrically. The success of the method for quantitative work depends upon obtaining a constant proportion of salicylic acid from the benzoic acid. Recently it has been observed that this constant proportion is not found when the whole of the solution, obtained as described (*loc. cit.*, p. 27), and containing very small quantities of benzoic acid, is oxidised. For example, 1 mgrm. of benzoic acid extracted from a foodstuff indicated rather less than 0·5 mgrm.; 2 mgrms. indicated slightly over 1 mgrm.; and 5 mgrms. indicated 4 mgrms. It has been shown that these differences are not due to incomplete extraction of the benzoic acid, but are to be attributed to

the test being carried out on a solution obtained by extraction from an immiscible solvent. In spite of the fact that the solution is boiled to remove the traces of dissolved solvent, something remains which reduces the proportion of benzoic acid converted into salicylic acid. If, instead of the immiscible solvent being extracted with alkali, the solvent is evaporated, the residual benzoic acid can be determined satisfactorily.

With this modification the method described (*loc. cit.*) gives a good colour with 1 mgrm. of benzoic acid, and even one-quarter of this quantity gives a perceptible tint when compared with a blank. It therefore appeared sufficiently delicate for the purpose in view.

CONVERSION OF BENZOYL PEROXIDE INTO BENZOIC ACID.—Flour which has been treated with benzoyl peroxide may contain part of the peroxide unchanged, and this must be converted into benzoic acid before the above method of determination can be applied.

Benzoyl peroxide is a remarkably stable substance, considering its composition. It can be heated with water and acids without decomposition, and it can be distilled unchanged in steam. It is insoluble in water, and while insoluble it is very resistant to oxidising and reducing agents. It dissolves in most organic solvents, and in these solutions its oxidising character is readily shown. For example, when it is dissolved in alcohol the addition of sodium hydroxide solution causes instant decomposition of the peroxide, the alcohol being oxidised to acetaldehyde and acetic acid in proportions varying with the conditions. That the reduction of the peroxide is practically instantaneous can be shown by diluting the alcoholic solution with water immediately after the addition of the alkali; no turbidity (due to insoluble peroxide) is produced. An interesting reaction is that obtained when acetone is the solvent. According to the conditions the oxidation of the solvent may proceed in one of the following ways:

$$(1)\quad 2CH_3COCH_3 + O_2 = 2CH_3CHO + 2HCHO$$

$$(2)\quad CH_3COCH_3 + O_2 = CH_3COOH + HCHO$$
$$= CH_3CHO + HCOOH$$

$$(3)\quad 2CH_3COCH_3 + 3O_2 = 2CH_3COOH + 2HCOOH$$

$$(4)\quad CH_3COCH_3 + 2O_2 = CH_3COOH + CO_2 + H_2O.$$

The principal factor affecting the reaction is the strength of the alkali used. By adjusting the conditions so that the reaction proceeds according to (1) the alkali used in combining with the only acid formed, *i.e.* the benzoic acid produced from the peroxide, is a measure of the peroxide originally present. This forms a rapid method of determining the strengths of commercial preparations containing benzoyl peroxide. The conditions are obtained by adding one volume of $N/10$ sodium hydroxide solution to one volume of acetone solution of benzoyl peroxide. Immediately after mixing, the solution should be diluted with four or five volumes of water to prevent reaction between the aldehydes and the alkali. The excess of alkali is determined by titration with $N/10$ acid, phenolphthalein being used as indicator. Provided the acetone and sodium hydroxide solution does

not stand for more than a minute or two before dilution, the reaction does not proceed measurably beyond equation (1) and is completely represented by

$$2\begin{matrix}C_6H_5CO\text{–}O\\ |\\ C_6H_5CO\text{–}O\end{matrix} + 4NaOH + 2CH_3COCH_3 = 4C_6H_5COONa + 2CH_3CHO + 2HCHO + 2H_2O$$

One ml. of $N/10$ sodium hydroxide solution $\equiv$ 0·0121 grm. of benzoyl peroxide.

For the purposes in view any extracted benzoyl peroxide was converted into benzoic acid by dissolving it in acetone and adding sodium hydroxide.

Isolation of Benzoyl Peroxide and Benzoic Acid from Flour.—Since both these substances are volatile in steam, a distillation process appeared most suitable, and it was found that in an acid calcium chloride solution 50 or even 100 grms. of flour could conveniently be distilled, yielding the whole of the peroxide or acid in about 300 ml. of distillate. From the distillate the peroxide and acid were extracted by an immiscible solvent; the peroxide was converted into acid as indicated above; oxidisable substances were removed by treatment with potassium permanganate, and the purified benzoic acid was extracted. It is at this stage that the immiscible solvent should be evaporated and the test for benzoic acid carried out on the residue. This applies to all determinations of benzoic acid by the method described (*loc. cit.*), irrespective of the solvent used or of the process of extraction.

Details of the Method.—About 40 grms. of calcium chloride and 100 ml. of water are placed in a litre flask; 50 grms. of the flour to be tested and 10 ml. of concentrated hydrochloric acid are added, and the flask is connected with a steam-distillation apparatus. Steam is passed, very cautiously at first, until the mass ceases to froth and becomes fluid, and then rapidly, the flask being heated to prevent increase in the bulk of the liquid. About 300 ml. of distillate are collected, saturated with common salt, and extracted twice with 50 ml. of ether. The ether is evaporated at a temperature of about 30° C., a rapid current of air being drawn over the surface. When the residue is practically dry 5 ml. of acetone are used to wash down the sides of the vessel and to dissolve the residue, and 5 ml. of 2 N sodium hydroxide solution are added. The mixture is diluted with an equal volume of water, and the acetone is boiled off. After the liquid has been cooled to 50 to 60° C. it is treated with permanganate solution until an excess is evident by the colour, when 10 ml. of 2 N sulphuric acid are added, and the solution is just decolorised by the addition of oxalic acid. Any insoluble fatty acids are filtered off, and the solution is extracted twice with about 20 ml. of a mixture of equal parts of ether and petroleum spirit. The extracts are evaporated to dryness, conveniently in a boiling-tube, at about 30° C., a current of air being drawn over the surface. When the last trace of solvent has disappeared any benzoic acid will be visible as a crystalline deposit. The residue is dissolved in 15 ml. of warm water, the solution is cooled, 1 ml. of iron solution (2·7 grms. $FeCl_3$+13 ml. of N sulphuric acid to 100 ml.), and 1 ml. of 0·1 per cent. hydrogen peroxide solution (1 ml. of 20 vol. hydrogen peroxide diluted to 60 ml. = 0·1 per cent.) are added, and the mixture is heated just to the boiling-point. After the addition of 0·5 ml. of N sodium hydroxide solution, the mixture is filtered while hot, and the precipitate is

washed with hot water until the filtrate measures 50 ml. To the cold filtrate one drop of iron solution is added, and the colour produced is matched by adding 0·01 per cent. salicylic acid solution to a solution obtained by adding the reagents to 15 ml. of water and completing the test as described above. The salicylic acid solution is standardised against the colour produced when the test is carried out on a known quantity of benzoic acid.

EXPERIMENTAL RESULTS.—Tests carried out on a number of untreated flours gave solutions indistinguishable from blanks. Flours to which either 1 mgrm. of benzoyl peroxide or 1 mgrm. of benzoic acid per 50 grms. had been added, gave colours equivalent to that obtained from 1 mgrm. of benzoic acid. A flour to which had been added ½ ounce of 25 per cent. benzoyl peroxide to 280 lbs. (= 1 part in 35,840) was tested, and duplicate determinations showed 1 part in 40,000 and 1 part in 33,000.

I wish to thank the Government Chemist for permission to publish this work.

GOVERNMENT LABORATORY,
LONDON, W.C.2

The Freezing-Point of Pasteurised and Sterilised Milks

BY G. D. ELSDON, B.Sc., F.I.C., AND J. R. STUBBS, M.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, October* 15, 1932)

DURING our discussions of the problems arising out of the freezing-point test for milk with various interested parties, we have received the impression that an opinion was fairly generally held that processes of pasteurisation and sterilisation, when applied to milk, tended to reduce the freezing-point depression.* We ourselves have found that, in certain cases, milks sold as pasteurised had a slightly higher freezing-point than the average, although not so high as to raise doubts as to the genuineness of the samples.

There does not appear to have been very much work done on this subject. Hortvet (*J. Ind. Eng. Chem.*, 1921, **13**, 198) refers to a paragraph in the fourth edition of Leach (p. 153), where it is stated that Gooren affirms that homogenising, pasteurising and sterilising have the effect of lowering the freezing-point. As regards pasteurising, Hortvet claims that this statement is wrong—the truth being that Gooren concluded that pasteurising sometimes changes the freezing-point, and sometimes does not. Monier-Williams (*Food Report to the Local Government Board*, No. 22, p. 24) found that sterilisation by heat causes a slight decrease in the freezing-point depression. Parker and Spackman (ANALYST, 1929, **54**, 220) found that the effect of pasteurisation was to cause a decrease of about 0·010° C.

* The symbol Δ is used to express the amount on the centigrade scale by which the freezing-point of milk is depressed below that of pure water when both determinations are done in the Hortvet apparatus operated according to the instructions laid down in the A.O.A.C., "*Methods of Analysis*," 3rd Ed., p. 219.

In order to settle the point as far as possible we arranged to carry out some experiments, and the following account is of results arising out of this work. By the courtesy of Lt.-Col. J. W. Brittlebank, C.M.G., of Allied Dairies, Ltd., Manchester, one of us was allowed to watch the whole process of the commercial sterilisation of milk and to take samples at various stages during the process.

The milk is poured from the churns, two churns at a time, into a large vat, where it is weighed, and from this, two samples, each of the milk from two mixed churns were taken. The milk is then flash-pasteurised, homogenised, and bottled. One of our samples was taken after each stage of the process. Two types of bottle are in general use—the crown-cork (which cannot be closed by ordinary means when once it has been opened) and the swing stopper, which can be opened and closed as many times as is desired. The dairy company in question strongly advise the use of crown-corks, and always supply this type unless the other (which they deprecate) is specially ordered. The crown-cork bottles are hermetically sealed before the sterilisation process is commenced, whilst the swing-stoppers are only loosely placed in position before heating, being tightened down afterwards while the bottles are still hot.

The process of sterilisation is carried out by heating in water (crown-corks) or steam (swing-stoppers) at a temperature of about 220° F. for half an hour.

Further samples were taken before the milk was heated, and also after heating and cooling. Some of these samples were taken, before and after heating, from the same bottle; others were taken from full bottles after heating, in order to check any possible effect of a partly-filled bottle on the result. The following results were obtained:

		Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ
Original milk (1)		12·5	3·8	8·7	0·543
,, ,, (2)		12·5	3·7	8·8	0·543
After flash pasteurisation		13·0	4·3	8·7	0·529
After homogenisation		12·6	3·8	8·8	0·543
From bottle before sterilisation	A	12·5	3·8	8·7	0·546
* ,, ,, after ,,	A				0·533
,, ,, before ,,	B	12·6	3·8	8·8	0·541
* ,, ,, after ,,	B				0·535
* ,, ,, after ,,		12·6	3·9	8·7	0·535
,, ,, before ,,		12·3	3·6	8·7	0·529
† ,, ,, after ,,					0·529
,, ,, before ,,		12·3	3·7	8·6	0·530
† ,, ,, after ,,					0·530
,, ,, before ,,		12·3	3·6	8·7	0·531
* ,, ,, after ,,					0·531

Samples marked * were from swing-stoppered bottles. Samples marked † were from crown-corked bottles.

In considering these results it must be remembered that the milks used were those supplied commercially to a large dairy, and that, although they were in the same condition as supplied by the farmer, their authenticity cannot be vouched for;

furthermore, owing to the nature and size of the plant used, it is quite likely that the samples taken at the various stages in the process were not part of the same original milk; in fact, the chemical analyses prove that such was the case. For our present purposes this is of no great consequence. The figures, as a whole, do not suggest that sterilisation has any material effect on the freezing-point of milk.

In order further to investigate the point, a series of experiments was commenced in the laboratory on Grade A, T.T., milks obtained from four different farms. Each sample was divided into three approximately equal portions; one was heated in a closed bottle in a water-bath at 65° C. for 30 minutes, another was heated in an autoclave (in a closed bottle) at about 220° F. for 30 minutes, whilst the third was untreated. On each of these portions the freezing-point was determined. The morning and evening milks of each farm were treated separately. The results obtained are set out in the following tables:

FARM A

Milk	Morning milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ	Evening milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ
Original	11·7	3·1	8·6	0·537	13·0	4·3	8·7	0·543
After pasteurisation				0·537				0·540
After sterilisation				0·536				0·534

FARM B

Milk	Morning milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ	Evening milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ
Original	12·0	3·1	8·9	0·542	12·7	4·0	8·7	0·534
After pasteurisation				0·540				0·532
After sterilisation				0·543				0·528

FARM C

Milk	Morning milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ	Evening milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ
Original	11·8	3·1	8·7	0·539	11·9	3·4	8·5	0·541
After pasteurisation				0·539				0·540
After sterilisation				0·539				0·539

FARM A (Two days later)

Milk	Morning milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ	Evening milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ
Original	11·5	2·5	9·0	0·542	12·4	3·9	8·5	0·543
After pasteurisation				0·542				0·540
After sterilisation				0·541				0·536

FARM B (Two days later)

Milk	Morning milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ	Evening milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ
Original	12·4	3·5	8·9	0·545	12·7	3·9	8·8	0·546
After pasteurisation				0·543				0·545
After sterilisation				0·543				0·545

FARM C (Two days later)

Milk	Morning milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ	Evening milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ
Original	11·8	3·2	8·6	0·541	12·3	3·9	8·4	0·538
After pasteurisation				0·540				0·538
After sterilisation				0·540				0·538

FARM D

Milk	Morning milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ	Evening milk: Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Δ
Original	11·9	3·1	8·8	0·539	12·3	3·8	8·5	0·544
After pasteurisation				0·539				0·543
After sterilisation				0·539				0·542

From the above results it will be seen that there is a slight tendency for the freezing-point depression to be decreased when the milk is heated. The amount of change, when it takes place, is, however, so small that it does not interfere with the value of the test when applied to milks which have been heated.

In order to put this opinion to a very severe test, a sample of Grade A, T.T., milk contained in a closed vessel, was heated in an autoclave for 30 minutes at about 230° F. This temperature is much higher than would ever be used in practice. The heated milk was quite brown in colour and had acquired a strong flavour, but the freezing-point depression had not been altered even under these very severe conditions.

THE LANCASHIRE COUNTY COUNCIL LABORATORY,
36, DANSIE STREET, LIVERPOOL

An Investigation into the Electrolytic Separation of Lead as Peroxide in Non-Ferrous Alloys

I. A NEW METHOD FOR THE DETERMINATION OF SMALL AMOUNTS OF LEAD IN COPPER AND COPPER-RICH ALLOYS

By B. JONES, M.Sc., F.I.C.

INTRODUCTION.—The accurate separation of small amounts of lead, of the order of 0·2 per cent. and under, in certain non-ferrous alloys has been shown in several communications to be a difficult matter. These small amounts are invariably present as impurities in commercial brasses and bronzes, and the methods generally recommended in most text-books for the determination of lead are, to say the least, highly suspect when dealing with these low concentrations of the metal. Most methods in metallurgical analysis depend upon the initial separation of lead as the sulphate, but this method suffers from the disadvantage that a long period of standing is essential for complete precipitation, while Dawkins and Weldon (*Proc. Soc. Chem. Ind.*, Victoria, 1922, **22**, 940) have shown that the solubility of lead sulphate in dilute sulphuric acid is sufficiently high to render inaccurate the determination of small quantities of lead by precipitation as sulphate unless the volume of solution is kept very small and a correction applied for this solubility. Attempts to diminish this solubility have been made by "fuming" the lead solution with sulphuric acid previously saturated with lead before diluting for precipitation, as recommended in Johnson's *Chemical Analysis of Special Steels*, etc., and by the addition of alcohol to the dilute sulphuric acid in low bulk. Fairhall (*J. Biol. Chem.*, 1924, **60**, 485), Francis, Harvey and Buchan (ANALYST, 1929, **54**, 725), and others, recommend the latter procedure for the separation of minute amounts of lead in urine; while the precipitation of lead sulphate in alcohol-water solution appears to be complete under these special conditions, this procedure is inadmissible in most metallurgical analyses, where it is generally recognised that the sulphate method of separation of small amounts of lead in the presence of large quantities of other metals is attended with serious errors. The initial separation of traces of lead as the sulphide or chromate is of little value in non-ferrous alloys owing to contamination with other metals. A much-improved method for the separation of traces of lead from various metals was evolved by Evans (ANALYST, 1928, **53**, 267), who, by means of a modified Reinsch reaction, separated the metal by percolation of the solution through copper filings, the deposited lead being dissolved in acetic acid, reprecipitated as chromate, and allowed to stand overnight. This method gives a complete separation of a small amount of lead, but all published methods dealing with the

determination of lead in small amounts in most materials require more than one working day for the determination of the metal.

PREVIOUS WORK ON THE ELECTROLYTIC DEPOSITION OF LEAD AS PEROXIDE.—The electrolytic method of removing lead from solution appeared to be hopeful as a means of improving upon other methods, especially as it would save time, and also avoids the introduction of other chemical reagents to facilitate the initial separation of the lead. The deposition of lead on an anode as the peroxide PbO_2 from a nitric acid solution in such materials as urine, foods, oils, and metallic alloys has been attempted by various investigators, with or without the previous separation of the metal as sulphide. The peroxide of lead is then either weighed direct on the anode after drying, or the electrolytic separation forms the first stage to a determination by other methods. A review of these electrolytic methods shows them to fall naturally into three classes:

(*a*) *Gravimetric.*—It is stated by Ibbotson and Aitchison (*Analysis of Non-ferrous Alloys*, p. 173) that one merit of the electrolytic process for the determination of copper in brass, etc., lies in the incidental provision which it makes for a sufficiently accurate determination of lead and manganese, which are deposited on the anode as peroxides. The copper is removed at a fairly high acidity, whilst the lead and manganese are deposited on the anode as peroxides. The manganese in the deposit is determined, calculated to MnO_2, which is deducted from the total weight on the anode, the difference being regarded as PbO_2, from which the lead percentage is calculated. It is admitted that the deposit is impure in any case, and the authors recommend an empirical factor for conversion of the peroxide to lead in place of the theoretical factor. Anon. (*Australia Munitions Supply Board*, 1926, Met., **6**, 1) separated the lead in copper by electrolysis; the deposit of PbO_2 was dissolved and the lead was precipitated as the sulphate, small amounts of lead being determined by weighing re-extracted lead sulphate. It has long been known that an empirical factor must be employed for the calculation of PbO_2 to Pb after drying the anodic deposit, owing to the tenacity with which water is retained by the peroxide. This varying factor depends upon the temperature of drying, the conditions of deposition, the amount of lead deposited, etc. The removal of the last traces of water is difficult (Sand, *Chem. News*, 1909, **100**, 269; Smith, *J. Amer. Chem. Soc.*, 1905, **27**, 1287; Fischer, *Z. Elektrochem.*, 1904, **10**, 945; Collin, ANALYST, 1929, **54**, 655; Nichols, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 384). Pamfilov and Blagonravona avoid the $PbO_2.H_2O$ error by converting the deposit into PbO by heating (*J. Russ. Phys. Chem. Soc.*, 1928, **60**, 699). Most of these methods, while apparently accurate when controlled, do not lend themselves to the determination of lead in commercial alloys, as they do not allow for the presence of large amounts of other elements. Glaze (*J. Ind. Eng. Chem.*, 1921, **13**, 553) determined small amounts of lead in brass by working on a factor weight (an empirical factor) of the material, and weighed the deposit of PbO_2 after drying at 210° C. for half an hour. He ignored, however, the presence of interfering metals such as manganese, arsenic, etc., while, in addition, it does not appear to be a good method to weigh a peroxide deposit which, in many samples, must weigh only a few milligrams on an anode many grams in weight. Many methods have been described (*Amer. Soc. Test.*

Materials, Annual Reports; Biltz, *Ber.*, 1925, **58**, 913; Rudolph, Măsl and Steyner, *Chem.-Ztg.*, 1928, **52**, 652; Smith, *Pulp and Paper Mag.*, 1928, **26**, 105; Haberland, *Chem.-Ztg.*, 1930, **54**, 346) where the simultaneous cathodic deposition of copper and the anodic deposition of lead as peroxide at fairly high acidity are recommended in such alloys as copper, brass, gun-metal, manganese bronze, etc.

It will be shown later that this procedure is to be deprecated, as the acidity and current density in the electrolyte require to be at different values for the quantitative deposition of the respective metal. Schrenk and Delano (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 27) states that the theoretical factor 0·8662 for the conversion of PbO_2 to Pb may be used, although other workers have recommended factors less than theoretical (*vide supra*), and that high results for lead are obtained only when interfering elements such as tin or bismuth are present. They state, however, that the lead-content of the solution should be more than 5 mgrms., and use an electrolyte containing 20–30 per cent. of nitric acid, together with a little sulphuric acid, for the deposition of the lead. The conditions specified are obviously unsuitable for the determination of small amounts of lead, as very erratic results are quoted if the solution contains less than 5 mgrms. of the metal. In addition, they state that certain metals and radicals interfere with the deposition, but make no provision to overcome the difficulty. Biltz (*loc. cit.*) states that when solutions of copper and lead are electrolysed simultaneously for the determination of both metals the PbO_2, which separates on the anode, is attacked by the nitrous acid formed, but he overcame this difficulty by starting the electrolysis in fairly strong acid concentration in the presence of urea, the electrolyte being afterwards diluted and the electrolysis continued.

(*b*) *Volumetric.*—Various volumetric determinations of the deposited PbO_2 have been attempted, to overcome the inherent inaccuracy involved in weighing the deposit. Bernhardt (*Z. anal. Chem.*, 1925, **67**, 97) dissolved the peroxide of lead in potassium iodide and ammonium acetate and titrated the liberated iodine with thiosulphate. MacInnes and Townsend (*J. Ind. Eng. Chem.*, 1922, **14**, 420) recommend an electro-volumetric method, whereby the peroxide of lead is dissolved in a standard solution of oxalic acid, the excess of which is titrated with potassium permanganate. They state that the deposit consists entirely of PbO_2 containing no higher oxides, and that the method given is more exact than weighing the deposit.

(*c*) *Colorimetric.*—The electrolytic separation of lead in foods, urine, etc., as a preliminary to a colorimetric determination has been utilised; the peroxide is dissolved from the anode, and the lead is determined as the sulphide (Francis, Harvey, and Buchan, *loc. cit.*), etc. The colours formed by the direct action of peroxide of lead on diphenylamine (Schmidt, *Deut. med. Woch.*, 1928, **54**, 520), on aniline, which is oxidised to aniline purple (Morgan, *J. Ind. Eng. Chem.*, 1919, **11**, 1055), and on tetramethyl-diamino-diphenyl-methane, which gives a blue colour (Klostermann, *Ver. Ges. deut. Naturforsch. Aerzte*, 1926, **3**, 1116; Petrow, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 311; Seiser, Necke and Müller, *Z. angew. Chem.*, 1929, **42**, 96), have been utilised for the determination of traces of lead in a solution comparatively free from large quantities of other metals, *e.g.* in foods, etc.

The general conclusion from a study of the literature seems to be that lead is a metal that is best removed electrolytically as peroxide from a solution containing large amounts of other ions, the separation being more quantitative and cleaner than the sulphate method if allowance is made for interference. For the determination of small amounts of lead the electrolytic gravimetric method that involves weighing the small deposit on an anode is unsatisfactory for the reasons stated, and there appears a definite need for a reliable method that will give accurate results with copper-rich alloys for amounts of lead of the order of less than 0·2 per cent., the separation of which from metals frequently associated with it in industrial alloys is a matter of concern. The electrolytic volumetric methods are not satisfactory for the determination of the small deposits of lead obtained, while the colorimetric methods published are suitable only where a trace (*e.g.* less than 1 mgrm.) of lead is to be determined, the accuracy diminishing for larger quantities, owing to the very deep colour formed with a lead-content greater than this critical value.

PRELIMINARY EXPERIMENTS.—Owing to the variable amounts of impurities found in different commercial alloys it is an advantage in metallurgical analysis to use a colorimetric method that will deal not only with a minute amount of the metal to be determined, but also with a few mgrms. with the same accuracy. I have already described such a method for the accurate determination of small amounts of lead in mineral acid solution (ANALYST, 1930, **55**, 318), where lead is determined colorimetrically from a nitric acid solution of the chromate, with or without the use of diphenylcarbazide indicator, depending on the lead-content. The preliminary experiments for the separation of a trace of lead from copper alloys were attempted at the suggestion of Mr. A. T. Etheridge (Woolwich), to whom I am indebted for advice and many helpful suggestions in the preliminary experiments. In order to ascertain the effect of varying acidity on the anodic deposition of small amounts of lead as peroxide, the following amounts of lead were taken, together with a solution containing 0·01 grm. of copper, and made up to a volume of 100 c.c., containing nitric acid at the acidities stated. The solution was electrolysed in the manner described later, and the lead-content of the deposit was determined colorimetrically, with the results given in Table I.

TABLE I

Lead taken Grm.	Lead recovered. Acidity of nitric acid in electrolyte: 1 Per Cent. Grm.	5 Per Cent. Grm.	10 Per Cent. Grm.	20 Per Cent. Grm.
0·0001	0·000097	0·00004	Nil	Nil
0·00025	0·00024	0·00005	Traces	Nil
0·0005	0·00048	0·0003	0·00005	Nil
0·0010	0·0010	0·00097	0·00076	Nil
0·0020	0·0020	0·0018	0·0008	Trace
0·0040	0·0040	0·0039	0·0037	0·0015
0·0050	0·0050	0·0049	0·0049	0·0020

These results prove that it is imperative that the acidity be kept at a low value for the determination of small amounts of lead, although almost quantitative

deposition of peroxide takes place even at 10 per cent. acidity when the solution contains more than 5 mgrms. of lead. These results confirm the work of Seiser, Necke and Müller (*loc. cit.*), who also obtained low results for lead at high acid concentrations; they also appear to show why a small quantity of lead cannot be accurately determined simultaneously with a large weight of copper, as the acidities for the quantitative electrolytic deposition of the two metals require to be kept at different values. Etheridge (ANALYST, 1924, **49**, 371) has shown that the best conditions for the quantitative deposition of copper in copper-rich alloys are an electrolyte containing a mixture of sulphuric and nitric acids, with the addition of small amounts of urea in the final stages of electrolysis to destroy any nitrous acid formed. The following experiment was carried out to test the accuracy of this process for the separation of small amounts of lead that may be deposited on the anode (in this case a gauze electrode):—Two grms. of electrolytic copper were dissolved in a mixture of 30 c.c. of (1 : 3) sulphuric acid and 5 c.c. of nitric acid (sp.gr. 1·42) in a 400-c.c. squat beaker. A small amount of lead (as nitrate) was added, and the solution was made up to 200 c.c. and electrolysed with a current of 4 amps., the gauze cathode being rotated. About 0·5 grm. of urea was added after 30 minutes, and when the solution was colourless the current was reduced by 0·5 amp. every 15 minutes down to 0·5 amp., 0·5 grm. of urea being added at each change. The anode was washed with the current on, and the lead was determined colorimetrically as described later. The following results were obtained. (A blank determination did not reveal any lead.)

Lead added, grm.	0·0005	0·001	0·003	0·005
Lead deposited, grm.	Nil	0·0003	0·0011	0·0034

These results prove that the determination of small amounts of lead is inaccurate under the conditions suitable for the determination of copper. The low results obtained cannot be ascribed to the formation of nitrous acid, as this acid was destroyed during electrolysis, but they prove that the deposition of small amounts of lead as peroxide requires a low nitric acid concentration. The following method was worked out to give accurate results for copper and copper-rich alloys containing less than 0·2 per cent. of lead.

GENERAL PROCEDURE.—*Preparation of the Solution.*—Three grms. of the sample are weighed out into a covered 400-c.c. squat beaker and dissolved by the addition of 20 c.c. of nitric acid (sp.gr. 1·2) and 10 c.c. of nitric acid (sp.gr. 1·42). If it is known that the lead-content of the sample is very low, as, *e.g.* in electrolytic copper or in some pure brasses, it is advisable to take a larger weight of sample (5 to 10 grms.), which is dissolved by the action of more nitric acid. The solution is evaporated rapidly to incipient crystallisation of copper nitrate (until the colour of the solution *just* changes from blue to green in most cases). If the sample contains much iron, however, care must be taken to prevent its precipitation, as the precipitate will be found difficult to re-dissolve in acid. If this happens it is best to repeat the experiment, care being taken to stop the evaporation in time. The beaker is then removed from the source of heat, and 3 c.c. of nitric acid (sp.gr. 1·42) are added from a burette. The cover and sides of the beaker are

washed down with warm water from a wash-bottle, and the beaker is heated gently until the copper nitrate is re-dissolved. If the solution is clear, it is made up to approximately 250 c.c. and cooled in running water, and is then ready for electrolysis.

Treatment of Alloys containing Tin and Antimony.—In the presence of tin and antimony there is a white turbidity or a white precipitate of the hydrated oxides in the final stage, due to precipitation by hydrolysis in the dilute acid solution. In this case the solution is made up to about 200 c.c. If only a turbidity is present, showing that the tin- or antimony-content is low, the electrolysis is carried out in its presence, but if a definite precipitate separates, as in the case of bronzes and certain brasses, etc., it must be removed by filtration and, owing to the absorptive properties of the precipitate, must be treated for any occluded lead. In high-tin alloys the oxide occludes practically all the phosphorus and arsenic present in the alloy. It has long been known that stannic oxide occludes practically every other metal in the alloy, and that a nitric acid attack of the sample never produces a pure stannic oxide. The precipitate is collected on a washed pulp filter, and is washed free from copper salts with a few small amounts of hot 5 per cent. ammonium nitrate solution. The pulp is transferred to a Kjeldahl flask of 200 c.c. capacity, and 10 c.c. of sulphuric acid (sp.gr. 1·84) are added together with 20 c.c. of nitric acid (sp.gr. 1·42). The flask is heated gently under a strong draught until the organic matter is destroyed, and then at a higher temperature until thick copious fumes of sulphur trioxide appear. This operation takes about 10 minutes and usually yields a clear solution, apart from a few crystals of ferric sulphate, if there is much occluded iron. If charring is persistent, it is easily dissipated by the addition of a few drops more of nitric acid, and by heating the solution again until fumes appear. If the tin oxide precipitate is very large (as in a large sample of certain tin bronzes) a further 10 c.c. of sulphuric acid will be required. The flask is then cooled, and the solution is diluted to about 50 c.c. with water and boiled gently to dissolve any ferric sulphate. Meanwhile a clear, warm solution of 20 grms. (or 30 grms. if 20 c.c. of sulphuric acid have been used) of A.R. sodium hydroxide (from sodium) is prepared in a 600-c.c. beaker, to which a few c.c. of a clear solution of sodium sulphide are added. The sulphuric acid solution is cooled somewhat, washed into a large tapped funnel, and run slowly into the warm soda, which is meanwhile agitated. The solution must be alkaline to litmus after the addition of the acid. There is invariably a dark precipitate of the sulphides of iron, copper, etc., which facilitates the precipitation of any trace of lead present. If a definite dark precipitate does not form (due to the purity of the stannic acid), it is advisable to add a few mgrms. of copper to produce a definite precipitate. The solution is heated to boiling, filtered through a thick pulp filter, and the precipitate is washed with hot 5 per cent. ammonium nitrate solution, once with 10 c.c. of hot sodium hydroxide solution, and, finally, washed free from sodium salts with hot 5 per cent. ammonium nitrate solution. (The tin and antimony may be recovered as the pure sulphides on acidifying the filtrate with hydrochloric acid.) The precipitate is dissolved by the addition of hot, dilute *aqua regia*, which is passed through the pulp three or four times, after which the pulp is washed with hot water. The solution is

evaporated to a syrup, 10 c.c. of nitric acid (sp.gr. 1·42) are added, and the solution is again evaporated, with the object of driving off every trace of hydrochloric acid. When incipient crystallisation of copper nitrate, etc., takes place in the final stage, the warm, clear, nitric acid solution of the sample (the filtrate from the stannic oxide precipitate) is added, and the whole is heated to boiling. The above procedure usually yields, by a single treatment, a clear separation of the impurities in stannic oxide from a large weight of tin and antimony, which are held in solution as their sodium thio-salts. If the treatment of the stannic oxide has not been done exactly as stated, there may be a trace of oxide left, which may be filtered off and ignored, but usually all the tin and antimony is removed. Fusion of stannic oxide with carbonates and flowers of sulphur, as recommended in many text-books, did not give good results, owing to incomplete separation of tin in one treatment.

ELECTROLYSIS.—The solution almost covers the electrodes, the beaker is covered with a split clock-glass, and electrolysis is carried out with a current of 2 amps. in the apparatus shown in the diagram. A higher current is not

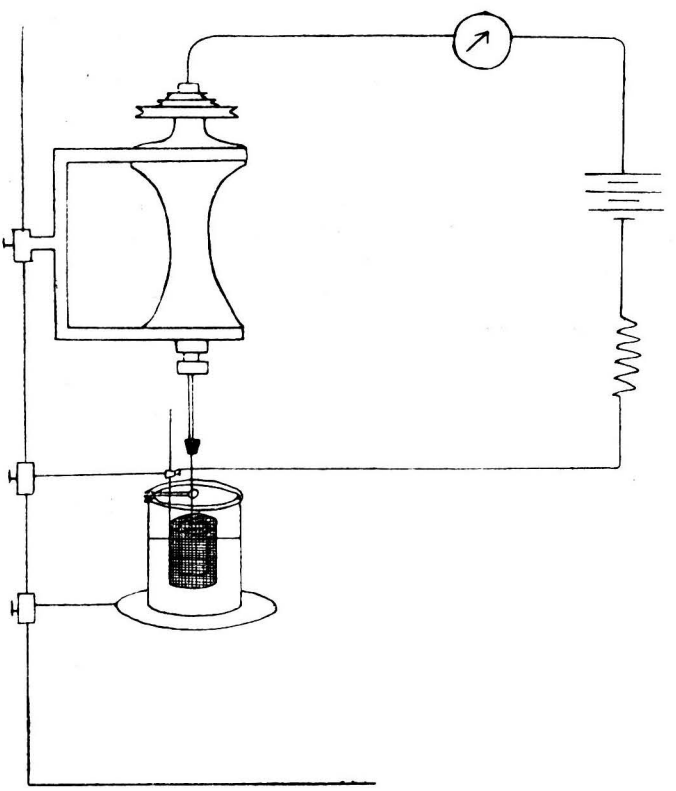

Fig. 1

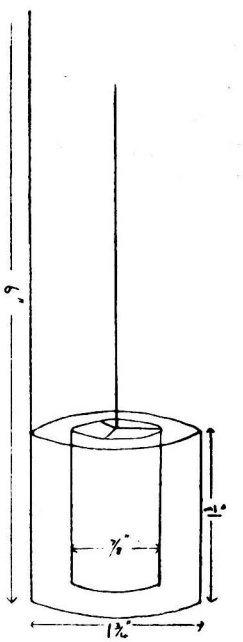

Fig. 2

recommended owing to the reduction of nitric acid in the electrolyte, the nitrous acid formed having a solvent effect on the deposited peroxide of lead.

So far as my experience goes, the quantitative deposition of lead as peroxide by electrolysis at a low current density is not disturbed by the formation of nitrous acid, and the addition of urea to destroy the acid is therefore unnecessary. A high current density will, in addition, induce the deposition of more copper on the cathode, thereby increasing the acidity of the electrolyte by the formation of more free nitric acid in the solution. The preliminary experiments were carried out by means of two platinum gauze electrodes kept half an inch apart, the anode being rotated. This arrangement was later replaced by two concentric electrodes of sand-blasted platinum gauze, as shown in the sketch Fig. 1, the inner electrode being the anode which is rotated at a speed of 400 R.P.M. This arrangement produces a uniform potential difference at all points of the electrodes, and gives very constant results. It is necessary to make the anode revolve at a fairly high speed, otherwise quantitative depositions of lead are not obtained. This suggests that the electrolysis itself is not sufficient to deposit all the lead as peroxide, but that the metal must be carried mechanically to the anode, where it is oxidised to the tetravalent state, the peroxide being probably pressed against the anode by anaphoresis, as suggested by Nicols (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 384). The source of the current may be a 10- or 20-volt circuit, provided with a rheostat of suitable resistance, or either two 2-volt accumulators joined in series. A suitable resistance for the latter would be in the form of a long wire provided with a sliding contact. The apparatus shown in the diagram is simple, and may be readily constructed in any laboratory. The grooved pulley attached to the upper end of the spindle to rotate the anode is driven by an electric motor (a small Meccano motor driven from the main circuit gives excellent results if only one electrolytic apparatus is in use, the motor being provided with a 60-watt lamp as a resistance). The electrolysis is carried out for 45 minutes; the beaker is lowered, and the electrodes are washed with a fine jet of water from a wash-bottle, the current being kept on during this process.

DETERMINATION OF THE LEAD.—The anode is disconnected and the deposit is dissolved by the addition of warm (1:1) hydrochloric acid, and washed with hot water into a small squat beaker. The peroxide, when not contaminated, is readily soluble in the acid, and in any case the anode must be stripped free from every trace of dark coloration. If the deposit contains a little manganese, bismuth, etc., it is less soluble in the acid. The clear solution is evaporated to a small bulk, and, finally, heated to dryness on a water-bath. Eight drops of (1:1) hydrochloric acid are added, and hot water to make a volume of approximately 50 c.c. The solution is heated until clear, and 10 c.c. of approximately $N/10$ potassium dichromate are added. The lead is precipitated as chromate in the manner that I described for the precipitation of small amounts of lead as chromate (*loc. cit.*), and the lead is determined colorimetrically by the method described, with or without the addition of the diphenylcarbazide indicator. If the copper or alloy is free from the interfering elements, described later, it is possible to complete a lead determination in about three hours.

TEST OF THE PROCESS.—The method has given very satisfactory results with certain commercial alloys. As a test for accuracy, small amounts of lead were

added to a solution of a sample of 3 grms. of electrolytic copper; the method of determination of the lead was then followed, with results as shown in Table II.

TABLE II

Lead added		$N/100$ $K_2Cr_2O_7$ required for comparison	Colorimetric reagent	Lead recovered	
Grm.	Per Cent.			Grm.	Per Cent.
Nil	—	<1 drop	5 c.c. of diphenyl-carbazide	—	—
0·0002	0·0066	0·3 c.c.	,,	0·0002	0·0066
0·0003	0·010	0·4 c.c.	,,	0·00028	0·0093
0·0005	0·0166	0·65 c.c.	,,	0·00045	0·0130
0·00075	0·025	1·0 c.c.	,,	0·00069	0·023
0·0010	0·033	1·4 c.c.	chromate colour compared	0·00097	0·032
0·0020	0·066	2·85 c.c.	,,	0·0020	0·066
0·0030	0·100	4·2 c.c.	,,	0·0029	0·097
0·0050	0·166	7·2 c.c.	,,	0·0050	0·166

Small amounts of lead were also added to a 10-grm. sample of electrolytic copper, and the lead was determined as above in order to prove the accuracy of the method.

The results are given in Table III.

TABLE III

Lead added		$N/100$ $K_2Cr_2O_7$ required for comparison c.c.	Colorimetric reagent	Lead recovered	
Grm.	Per Cent.			Grm.	Per Cent.
Nil	—	0·15	5 c.c. of diphenyl-carbazide	0·0001	0·001
0·0001	0·001	0·3 =0·15	,,	0·0001	0·001
0·0002	0·002	0·35=0·20	,,	0·00014	0·0014
0·0005	0·005	0·8 =0·65	,,	0·00045	0·0045
0·001	0·010	1·45=1·3	chromate colour compared	0·0009	0·009
0·002	0·020	3·05=2·9	,,	0·0020	0·020
0·004	0·040	5·85=5·7	,,	0·0039	0·039
0·005	0·050	7·4 =7·25	,,	0·0050	0·050

The method has been proved to give good results with commercial brasses and bronzes which do not contain elements that interfere with the quantitative deposition of the lead, either by inhibiting the reaction or by occlusion on the anode. Interfering elements present in special copper alloys require modifications of the method, which are described later. Results obtained with various alloys are given in Table IV. The method, although specially designed to determine less than 0·2 per

cent. of lead, may be extended to determine larger amounts by taking a sufficiently small weight of the sample and adding electrolytic copper to make a total sample weighing 3 grms. With these alloys containing appreciable quantities of lead it is important, however, that not more than 0·005 grm. of lead (as peroxide) is deposited on the anode, otherwise inaccurate results will be obtained. This is due to the necessity of using a higher acid concentration, and also because the sensitiveness of the colorimetric method diminishes when larger amounts of lead are determined as chromate.

TABLE IV

Percentage composition of alloy	Pb added Per Cent.	†Pb reported by $PbSO_4$ method Per Cent.	Pb found by this method Per Cent.
Copper, 95; iron, 5	0·04	—	0·04
Copper, 70; zinc, 29; iron, 0·2	—	0·072	0·096
Copper, 60; zinc, 38·5; iron, 0·6	—	Traces	0·042
Copper, 51; zinc, 38; iron, 3; nickel, 5	—	Traces	0·022
,, ,, ,, ,,	0·10	—	0·120
Copper, 69·4; zinc, 21·8; iron, 0·2; nickel, 4; aluminium, 5	—	0·10	0·12
Copper, 85; iron, 5; aluminium, 9·7	—	Nil	0·014
,, ,, ,,	0·020	—	0·032
Copper, 60; nickel, 40	0·080	—	0·080
Copper, 88; tin, 11·5	—	Nil	0·060
Copper, 89; tin, 5; antimony, 3	—	Traces	0·09
Copper, 96; magnesium, 4	0·10	—	0·10
Copper, 98; chromium, 2	0·070	—	0·065
Copper, 99; vanadium, 1	0·10	—	0·10
Copper, 99; boron, 1	0·10	—	0·08
Copper, 90·0; tin, 9·0; phosphorus, 0·5	—	Nil	0·042
,, ,, ,,	0·10	—	0·140
Copper, 76; zinc, 19*	—	2·70	2·77
Copper, 81; tin, 4·5; zinc, 8*	—	6·50	6·35

* Small weight dissolved for analysis with electrolytic copper to make a 3-grm. sample.
† By another analyst.

It will be seen that the method can be carried out in the presence of most of the elements present in the commercial alloys of copper, but alloys used for certain special purposes contain elements that interfere with the process. The method then requires modification which generally necessitates the removal of the interfering elements.

MODIFICATIONS OF PROCESS DUE TO THE PRESENCE OF INTERFERING ELEMENTS

Tin and Antimony.—These are removed by hydrolysis from the nitric acid solution; any occluded lead is recovered by the method described.

Manganese is oxidised to permanganic acid by the oxygen evolved at the anode during electrolysis. If there is more than 1 per cent. present, the pink permanganate colour imparted to the electrolyte is destroyed during the latter stage

of electrolysis by the formation of hydrated manganese dioxide, part of which is co-deposited with the lead on the anode, but most of which floats about the beaker as a brown slime; both these effects are undesirable. If more than a centigram of manganese is co-deposited with the lead it will interfere with the precipitation of the metal as chromate, as it will precipitate as hydroxide on neutralising the solution with ammonia and the precipitate will not redissolve on the addition of acetic acid. If less than a centigram of manganese is deposited this will not interfere with the precipitation as chromate, as it is retained in solution by the ammonium chloride generated in the liquid. Attempts were made to separate the lead from copper and manganese by adding 0·1 grm. of iron to the solution and occluding the lead in ferric hydroxide by precipitation with ammonia; after a re-precipitation of the iron from hydrochloric acid solution and solution in nitric acid containing 3 grms. of electrolytic copper, the ordinary process was followed. This procedure gave a solution which did not contain sufficient manganese to interfere, but low results for lead were obtained, and experiments on this line were discontinued. Attempts to remove manganese as peroxide from nitric acid solution by electrolysis or by the addition of sodium bismuthate, potassium chlorate, etc., before electrolysis for lead were unsatisfactory, owing to erratic results being obtained by co-deposition or to the presence in the electrolyte of interfering elements. Ultimately it was found possible to carry out the method described below in the presence of manganese in alloys containing less than 2 per cent. of manganese. In alloys containing more than 2 per cent. of manganese the interference of the metal is too great, owing to the difficulty of preventing the formation of peroxide of manganese, a large amount of which is formed in the high manganese alloys.

(*a*) METHOD FOR COPPER ALLOYS CONTAINING LESS THAN 2 PER CENT. OF MANGANESE.—Most of the alloys known as manganese brass, manganese bronze, high tensile aluminium-iron-manganese brass, etc., contain less than 2 per cent. of manganese, and are treated as follows:—The usual method is followed exactly as described up to the stage of electrolysis. The presence of manganese will be revealed soon after the commencement of electrolysis by a pink colour in the electrolyte, and some manganese will be deposited on the anode if this is allowed to persist throughout the electrolysis. It is dissipated by the cautious addition of a 50 per cent. solution of hydrazine nitrate, drop by drop, until the liquid regains the blue colour, and the electrolysis is continued. Care must be taken that not more of the hydrazine salt is added than is required to reduce the permanganate colour; the permanganate formed must not be allowed to decompose into peroxide of manganese, as a larger quantity of hydrazine will be required to dissipate the precipitate, which will also occlude some of the lead if it persists. During the electrolysis more permanganate will probably be re-formed from time to time, but it is readily cleared with a couple of drops of the hydrazine solution. The presence of the permanganate colour itself does not seriously interfere with the deposition of the lead, so long as peroxide of manganese is not formed by its decomposition. A small amount of manganese peroxide on the anode also does not interfere with the determination of the lead as chromate. The deposit on the anode is stripped and the lead is determined as described previously.

Results obtained are shown in Table V.

TABLE V

Alloy	Composition	Lead added Per Cent.	Lead found by lead sulphate method Per Cent.	Lead found by this process Per Cent.
Aluminium manganese brass	Copper, 57; iron, 0·1; manganese, 1; aluminium, 1·4; zinc, 40.	—	Nil	0·023
,,	,, ,,	0·05	—	0·070
Aluminium, iron, nickel, manganese brass	Copper, 56; iron, 1·5; manganese, 1·5; aluminium, 1·5; nickel, 3; zinc, 36·5.	—	0·16	0·18
Manganese brass	Copper, 58·6; iron, 1·5; manganese, 1·9; tin, 0·1; zinc, 37.	—	0·06	0·11
Manganese brass	Copper, 60; iron, 0·9; manganese, 2·0; tin, 0·08; zinc, 37.	—	Nil	0·045
,,	,, ,,	0·10	—	0·142
Manganese bronze	Copper, 58; iron, 2·4; manganese, 1; tin, 0·5; zinc, 38.	—	Traces	0·086

(*b*) METHOD FOR COPPER ALLOYS CONTAINING MORE THAN 2 PER CENT. OF MANGANESE.—Three grms. of the sample are dissolved in 25 c.c. of nitric acid (sp.gr. 1·2) and 10 c.c. of nitric acid (sp.gr. 1·42). The solution is diluted to 200 c.c. and, if fairly clear, the copper is removed from the solution electrolytically. If there is a precipitate of tin oxide at this stage, denoting a large amount of tin in the alloy, it is filtered and retained. The copper is deposited on the inner rotating electrode, which is made the cathode by reversal of the circuit. The electrolysis is carried out with a current of 3 to 4 amps., when most of the copper is deposited in about one hour, as shown by the solution becoming almost colourless. With alloys containing a large amount of manganese there will be a permanganate coloration even at this high acidity, but there will not be as great a tendency to form a large precipitate of manganese peroxide as by electrolysing at low acidity. Any pink coloration is easily dissipated by the addition of a few drops of 50 per cent. hydrazine nitrate. It is not essential to remove the total copper, but to continue only until the electrolyte is almost colourless. The electrodes are then washed with water, the washings being collected in the beaker, the whole contents of which are then boiled for about 10 minutes. The deposited copper is dissolved in nitric acid and retained. The anode, on which may have been deposited a trace of manganese, is immersed in 20 c.c. of warm hydrochloric acid, and is washed lightly before withdrawal. Electrolytic iron, or low carbon steel (0·1 grm.) is added to this hydrochloric acid, and when it has dissolved, 10 c.c. of nitric acid (sp.gr. 1·42) are added to the solution. This solution is put into the beaker containing the electrolyte, which is then boiled for a few minutes to ensure a thorough oxidation. The solution is made alkaline with (1:1) ammonia, and heated to boiling. (If the alloy contains sufficient elements to yield an appreciable precipitate with ammonia it may be unnecessary to add the 0·1 grm. of iron, but with most alloys it is advisable to add it.) The hydroxides of iron, manganese, etc., are filtered through a

No. 41 Whatman paper, and the precipitate is washed just free from copper with hot water and dissolved in 60 c.c. of boiling (1:1) hydrochloric acid. The iron is re-precipitated with ammonia; the precipitate is filtered off and washed free from chloride. It is dissolved in hot nitric acid (sp.gr. 1·2) containing 2 to 3 drops of sulphurous acid, and this solution is added to the nitric acid solution containing the copper (previously deposited on the cathode), which is then evaporated to incipient crystallisation; three c.c. of nitric acid (sp.gr. 1·42) are added, and the solution is diluted and electrolysed for lead. If tin oxide is precipitated at this stage it is filtered off with any previous oxide, and if the precipitate is large any occluded lead is recovered as described. The lead is then determined in the usual way. During the electrolysis for lead there is occasionally a slight tinge of permanganate coloration formed if a little manganese is still retained. This is easily cleared with a drop of hydrazine nitrate solution, and it is never sufficient to interfere with the process. This modification of the process is necessary for the separation of small amounts of lead in such alloys as manganese copper, manganese nickel brass, manganin, etc. By this means the whole of the lead is occluded in the iron hydroxide precipitate, which is rendered free from manganese by a re-precipitation from mineral acid solution, manganese being retained in solution by the ammonium chloride generated. If copper is not removed electrolytically prior to precipitation of the iron, etc., an unsatisfactory filtration results, and low results for lead are obtained. The method was tested by adding known amounts of manganese nitrate to 3 grms. of electrolytic copper, with results shown as follows:

Amount of manganese added as manganese nitrate		Lead added		Lead recovered		
					Less blank	
Per Cent.	Blank Grm.	Grm.	Per Cent.	Grm.	Grm.	Per Cent.
10	0·0002	0·003	0·10	0·0031	=0·0029	0·097
20	0·0004	0·001	0·033	0·0014	=0·001	0·033
20	0·0004	0·003	0·10	0·0032	=0·0028	0·093
20	0·0004	0·005	0·17	0·0055	=0·0051	0·17

Arsenic, when present in more than small amounts, retards the deposition of lead peroxide, owing to the presence in the electrolyte of arsenious acid, appreciable amounts of which inhibit the deposition. Low results are obtained in alloys containing more than 0·1 per cent. of arsenic as shown:

Sample (3 grms.)	Arsenic added Per Cent.	Lead added Grm.	Lead found		
			Blank Grm.	Less blank	
				Grm.	Grm.
Electrolytic copper	Nil	0·003	0·0001	0·0030	=0·0029
,, ,,	0·10	0·002	—*	0·0015	
,, ,,	0·17	0·003	—*	0·0015	
,, ,,	0·50	0·003	—*	0·0065	
,, ,,	0·66	0·004	—*	0·0008	
,, ,,	5·0	0·005	—*	0·0013	

* Too small to be detected owing to the presence of the arsenic.

This proves that erratic results will be obtained in the analysis of such materials as arsenical bronze, loco fire-box plates, etc., which contain about 0·5 per cent. of arsenic. It is, therefore, essential to remove the arsenic before

the lead is determined; this was attempted by distillation, but results obtained were not satisfactory, and the only modification of the method that gave reliable results was the electrolytic separation of the copper and the subsequent removal of arsenic by solution in alkaline sulphide.

METHOD FOR COPPER ALLOYS CONTAINING ARSENIC.—Three grms. of the sample are dissolved in 20 c.c. of nitric acid (sp.gr. 1·2), and 10 c.c. of nitric acid (sp.gr. 1·42), the solution is diluted to 200 c.c. and, if clear, is electrolysed, the copper being deposited on the inner rotating electrode, which is made the cathode. (Any tin oxide that separates in high tin alloys will occlude much of the arsenic, and is treated for the recovery of any lead as in the usual method, the tin and occluded arsenic being removed as soluble sulpho compounds.) The electrolysis is carried out with a current of 3 to 4 amps., and is stopped when the electrolyte is colourless. Some of the arsenic will be evolved at the cathode as hydrogen arsenide during the electrolysis. The deposited copper is dissolved in nitric acid and retained until later. The anode is immersed in a few c.c. of warm hydrochloric acid, which is added to the solution from which the copper has been removed. This solution is added gradually to a clear solution containing 20 grms. of sodium hydroxide (A.R.), together with a little clear sodium sulphide solution, which is stirred during the addition. A dark precipitate will be formed of the sulphides of copper, iron, etc., which will collect the small amount of lead sulphide. Care must be taken that the solution is now alkaline in order to keep arsenic in solution. The solution is heated to boiling and filtered through a thick pulp filter; the precipitate is washed with hot 5 per cent. ammonium nitrate solution, then once with a small amount of hot 20 per cent. sodium hydroxide solution, and finally washed free from alkali. (The arsenic will be revealed, on acidifying the filtrate with hydrochloric acid, as yellow clots of sulphide.) The precipitate is dissolved in hot dilute *aqua regia*, which is passed through the pulp 3 or 4 times, and the pulp is then washed free from acid with hot water. The solution is evaporated to a paste, a small volume of nitric acid (sp.gr. 1·42) is added, and the solution is again evaporated to a paste to drive off all trace of hydrochloric acid. The nitric acid solution (containing the cathode copper) is now added, and the whole is evaporated to incipient crystallisation of copper nitrate, after which the usual electrolytic process is followed, the lead being deposited as peroxide from a solution without interference of arsenic. The following results were obtained with samples of electrolytic copper to which known amounts of arsenic were added, and with samples of arsenical coppers:

Sample (3 grms.)	Arsenic added or present Per Cent.	Blank Grm.	Lead added		Lead recovered		
			Grm.	Per Cent.	Less blank Grm.	Grm.	Per Cent.
Electrolytic copper	0·30	0·0003	0·003	0·10	0·0031	=0·0028	0·070
,, ,,	0·50	0·0003	0·002	0·066	0·0021	=0·0018	0·060
,, ,,	0·50	0·0003	0·005	0·166	0·0052	=0·0049	0·163
*Arsenical copper, A	5·0	0·0003	—	—	0·0027	=0·0024	0·080
,, ,,	,,	0·0027	0·003	0·10	0·0055	=0·0028	0·093
*Arsenical copper, B	37·0	0·0003	—	—	0·0012	=0·0009	0·030
,, ,,	,,	0·0012	0·002	0·066	0·0031	=0·0019	0·063

* Alloys supplied by Prof. A. A. Read.

Phosphorus.—The process gives good results with alloys containing less than 0·5 per cent. of phosphorus, but a larger amount produces low results for lead, owing to the presence of appreciable amounts of phosphoric acid in the electrolyte. Most brasses and phosphor bronzes contain less than this amount of phosphorus, and alloys containing more than 1 per cent. of phosphorus are rarely encountered. It is permissible to remove the phosphorus from a dilute nitric acid solution as ammonium phosphomolybdate by the addition of a small amount of ammonium molybdate solution.*

The yellow precipitate is allowed to settle and the liquid is filtered through pulp, which is then washed with 2 per cent. nitric acid. The filtrate is evaporated to a small bulk, and the usual method is followed for the determination of lead. Care must be taken during the evaporation, as the excess of ammonium molybdate yields a white precipitate of molybdic acid, which will cause bumping. With alloys containing less than 1 per cent. of phosphorus the addition of 10 to 15 c.c. of ammonium molybdate is sufficient, and larger amounts are added in proportion to the phosphorus-content. With phosphor bronzes containing a high percentage of tin, practically the whole of the phosphorus will be occluded in the stannic oxide (precipitated by hydrolysis), probably as stannic phosphate; the precipitate is treated for the recovery of any lead as described previously, and the lead is separated from the tin and phosphorus. With these high-tin alloys the addition of ammonium molybdate to the filtrate from the stannic oxide is unnecessary. Results obtained with various samples are as follows:

Sample (3 grms.)	Phosphorus Per Cent.	Blank Grm.	Lead added		Lead recovered		
			Grm.	Per Cent.	Grm.	Less blank Grm.	Per Cent.
Copper-phosphorus alloy	0·5	—	—	—	0·0005		0·017
,, ,,	,,	0·0005	0·0020	0·066	0·0024=0·0019		0·063
,, ,,	,,	0·0005	0·0030	0·10	0·0032=0·0027		0·090
Phosphor bronze	0·97	—	—	—	0·0012		0·040
,, ,,	,,	0·0012	0·0020	0·066	0·0032=0·0020		0·066
,, ,,	0·76	—	—	—	0·0028		0·093
,, ,,	0·82	—	—	—	0·040		0·133

Bismuth.—Small amounts of bismuth, as found in some copper alloys, do not interfere with the process. When bismuth is present, the lead peroxide deposit will be contaminated therewith, and somewhat erratic results for lead will occur if the alloy contains more than 1 per cent. of bismuth. This is due to the formation of bismuth oxychloride on stripping the deposit and in the precipitation stage of converting the lead into chromate. This prevents a crystalline precipitate of lead chromate, and produces a slimy mixture of chromate and oxychloride. Bismuth is so rarely present as a constituent that a detailed process for its separation in copper alloys has not been attempted.

Silver, when present, occurs only as a trace in most commercial alloys, and does not interfere, but in alloys containing silver as a constituent, *e.g.* coinage

* Solution made by dissolving 50 grms. of ammonium molybdate in 95 c.c. of water, plus 38 c.c. of ammonia (sp.gr. 0·88) and poured into 470 c.c. of nitric acid (sp.gr. 1·2).

alloys, etc., a colloidal precipitate of the metal is formed in the dilute acid before electrolysis. The metal induces an uneven deposition of lead as peroxide on the anode, and is also deposited on the cathode with the copper, preventing an adherent deposit of the copper.

Acknowledgments and thanks are due to Prof. A. A. Read, D.Met., for granting facilities to carry out the experiments described, and for permission to publish the results.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A METHOD OF DETERMINING IODINE IN ORGANIC COMPOUNDS CONTAINING SELENIUM

FRERICHS pointed out that when chlorine in organic compounds containing selenium is determined by the method of Carius, the silver chloride is accompanied by silver selenite. He described a method for separating silver halide and silver selenite, whereby both the selenium and the halogen might be determined, but he recorded that the halogen values are always higher and the selenium values always lower than those calculated (*Arch. Pharm.*, 1902, **240**, 656). Modifications of Frerichs' method for estimating selenium have been described (Becker and Meyer, *Ber.*, 1904, **37**, 2550; Vanino and Schinner, *J. prakt. Chem.*, 1915, **91**, 116) but these do not deal with the method for determining halogen in the presence of selenium.

In connection with new cyanine dyes containing selenium, a method of determining the iodine-content, in order to confirm the purity, was required. The following simple method for determining iodine has been found suitable, and is doubtless also applicable to the determination of other halogens:

The substance (0·2 grm.) is heated with fuming nitric acid (40 drops), which is free from halogen, and with silver nitrate (about 0·5 grm.) in a sealed tube at 300° C. for some hours, according to the well-known method of Carius.

On the following day the contents of the tube are washed into a beaker with water, and the mixture is boiled for an hour. While still hot, so that the silver selenite is retained in solution, the liquid is filtered through a Gooch crucible, the silver iodide being washed into the crucible with cold water, and subsequently well washed in the crucible in order to remove silver nitrate. Then 100 c.c. of nearly boiling 20 per cent. nitric acid (20 c.c. of acid of sp.gr. 1·42 in 100 c.c.) are slowly drawn through the crucible, in order to remove any remaining silver selenite. After this, the precipitate of silver iodide is washed with water, dried at 110° C., and weighed. The weight of the empty crucible is best obtained by dissolving out the silver iodide with potassium cyanide, washing, drying, and weighing. The

following results show the order of accuracy obtainable in the case of quaternary salts and dyes which contain selenium as well as iodine:—

(1) For 1-methyl-benzselenazole methiodide, found: I=37·50 per cent., 37·69 per cent. ($C_9H_{10}NISe$ requires I=37·53 per cent.).

(2) For 1-methyl-benzselenazole ethiodide, found: I=36·21 per cent. ($C_{10}H_{12}NISe$ requires I=36·04 per cent.).

(3) For 2:2′-dimethyl-seleno-tricarbocyanine iodide, found: I=20·64 per cent. ($C_{23}H_{21}N_2ISe_2$ requires I=20·79 per cent.).

(4) For 2:2′-diethyl-seleno-tricarbocyanine iodide, found: I=20·07 per cent. ($C_{25}H_{25}N_2ISe_2$ requires I=19·86 per cent.).

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THE HORTVET CRYOSCOPE

WE have read the very interesting paper by H. C. Lockwood (ANALYST, 1932, **57**, 698) on the use of the Hortvet cryoscope—a piece of apparatus rapidly becoming an indispensable equipment for all who are engaged in the analysis of milk.

While we fully appreciate the ingenious device which Mr. Lockwood adopts in the endeavour to avoid errors due to parallax when reading the thermometer, the question arises whether the increased accuracy which such an arrangement may secure is sufficient to outweigh the disadvantages due to increasing complication.

For our own part, we have never adopted the use of the rather large long focus lens with the loose universal movement supplied with the apparatus (*cf.* also D. Henville, ANALYST, 1932, **57**, 569), and, as a matter of fact, it was omitted at our own request from the last stand we purchased. We have both used the Hortvet cryoscope very frequently during a period of several years, and are fully convinced that all that is necessary for reading the thermometer with a sufficient degree of accuracy is a good pocket lens. We prefer one with a diameter of about 19 mm., which is in focus when about 43 or 44 mm. from the thermometer. We have found that after a little practice it is quite possible and usual for two observers to make absolutely uniform readings of the same position of the mercury.

For those who are new to this particular operation and who, before they have attained complete confidence, find difficulty in avoiding errors due to parallax, we can recommend, after repeated trials, the "Magnifying Reader," listed on page 220 of the current catalogue of Messrs. Griffin & Tatlock. We are convinced, however, that after a very short time the majority of observers will turn to the small hand-lens as the most convenient, quick and sufficiently accurate means of reading the temperature.

We note that Mr. Lockwood seems to regard it as a disadvantage that he is unable to continue the stirring while he is tapping the thermometer. Whilst at the moment we do not wish to lay down hard and fast rules or express any final opinion as to the exact amount or rate of stirring which is necessary or desirable, we should like emphatically to draw the attention of workers to what appears to us the extreme desirability of following, as far as possible, the method of procedure laid down by the American A.O.A.C. In this connection they recommend a very modest amount of stirring, the exact words being: "Manipulate the stirrer slowly and carefully 3 or 4 times as the Hg column approaches its highest point." We maintain that there is no object in deviating from this unless some special and obvious advantage is gained.

We have ourselves adopted a mechanical stirrer driven by a small electric motor, which we find very satisfactory. By having two switches on the right-hand side of the wooden stand, one for the stirrer and the other for an electric blower (Gallenkamp, Catalogue No. X, 1050), the whole operation becomes very easy to control.

We have from time to time had in mind the possibility of adopting variations both in the apparatus and mode of procedure, and we have tried several, but in no instance, so far, have such innovations been justified, in our opinion, on the grounds of increased accuracy or speed. The cryoscope, as designed by Hortvet, and worked in accordance with his instructions, is a simple and efficient apparatus, and we would suggest that it be adopted without essential modifications, for by this means it will be secured that all observers will carry out the test under conditions as far as possible identical, and thus arrive at comparable results.

With regard to the question of preserving samples for two or three days, we would call attention to the work of R. Rüdiger (*Chem.-Ztg.*, 1932, **56**, 533; ANALYST, 1932, **57**, 578), who finds that 0·01 per cent. of mercuric chloride will preserve milk kept at 25° C. for three days, and that the temperature correction for the addition is 0·002° C.

We would also like to mention the fact that many sets of apparatus have been put on the market which do not conform with Hortvet's specification in all respects, more particularly with regard to the size of the Dewar flask. This point is at present under investigation by the manufacturers.

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THE DETECTION OF FREE METAL PARTICLES IN DUST, ETC.

THE detection of metallic fragments in dust, sand, sludge, etc., is often of importance, and this is not always a simple matter when the oxides or salts of the metal are also present. The following method is readily carried out, and may be made roughly quantitative if necessary.

No preliminary treatment is required if the material examined is free from grease, resin and chlorides, but if these are present, a few milligrams of the sample may be shaken with three small portions of ether followed by three washings with alcohol, after which the residue should be washed with water. In some cases washing with cold 1 per cent. sodium hydroxide solution will serve to remove interfering organic substances, the alkali being subsequently removed by washing with water.

A small portion of the original (or purified) material is transferred to a glass microscope slide and moistened, if necessary, with a drop of water; this is followed by two drops of approximately 1 per cent. silver nitrate solution, which are mixed with the powder, and, after a few minutes, the mixture is examined under a low magnification.

Each particle of free metal gives rise to the formation of a silver "tree" which may be readily identified, and if the metallic fragments are not too numerous a quantitative "count" may be made of the number present.

This method has been found to yield satisfactory results with copper, mercury, bismuth, lead, zinc, aluminium, and magnesium; and although, theoretically, equally reliable results should be obtained with tin and iron, for some unexplained reason these two metals occasionally fail to produce any deposition of silver in the "tree" form.

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THE ACTION OF ULTRA-VIOLET LIGHT ON GELATIN IN PAPER

WHEN a tub (gelatin)-sized paper of good quality, free from resin, is irradiated by the light of a quartz mercury lamp it rapidly loses its property of ink resistance, with degradation of the surface colour to a brown shade. That this effect is not wholly or partly due to the formation of ozone or other peroxides in the air of the cabinet is indicated by its occurrence when the paper is shielded by the interposition of a quartz plate with exclusion of air. The action of the light is accelerated if the paper is kept damp. The "browning" is seen to be a function wholly or mainly of the gelatin, since cellulose properly prepared suffers little or no change in colour under these conditions.

References to the phenomenon in the literature are lacking, but it seemed probable that the gelatin molecule suffers some sort of degradation rather than any physical change (viscosity, etc.). As in paper the reaction does not proceed easily to finality, owing to the considerable screening effect exerted by the discoloured gelatin in massive concentration, an attempt was made to irradiate a dilute solution (0·3 per cent.) of gelatin in water. Fifty ml. of this solution were exposed in a porcelain dish, $4\frac{1}{2}'' \times 3\frac{1}{2}''$, at a distance from the lamp of approximately 10 cm. The lamp was further screened by the interposition of a 2 mm. quartz plate to avoid the too rapid evaporation caused by draught from the heat of the lamp. The temperature of the air immediately below the lamp in these circumstances was 53° C. Any water vaporised was replaced from time to time. After some hours there was a certain amount of discoloration of the solution, and this had an odour resembling caramel. No ammonia was detected in the vapour evolved, and tests for hydroxylamine gave negative results. The original p_H value of 6·6 was depressed after five hours to 6·1.

The final product, made up to original volume, continued to give the usual protein reactions with tannic and picric acids, chlorine water, phosphotungstic acid, etc., but in all cases the precipitates were much reduced in bulk. Satisfactory examination of the irradiated product was practically impossible by reason both of the small quantity available and of the incompleteness of the process, but no reactions characteristic of the usual hydrolysis products of gelatin have been observed. The product does not reduce Fehling's solution, and no evidence of the presence of peroxides could be obtained.

The solid matter left on evaporation of the solution amounted to 0·16 per cent., and was soluble in a small quantity of warm water to form a golden brown solution which would no longer gelatinise.

In all the circumstances it seems likely that the degradation of gelatin under the influence of ultra-violet light, and in the conditions described, is directed towards the formation of compounds of the simplest type.

H. A. BROMLEY

H.M. STATIONERY OFFICE LABORATORY

Official Appointments

THE Minister of Health has approved the following appointments:

F. G. D. CHAMBERS as a Public Analyst for the County Borough of Coventry, in addition to W. J. Rigby, who has been approved as Senior Analyst in place of A. Bostock Hill (deceased) (December 16th, 1932).

D. J. T. BAGNALL, F.I.C., as a Public Analyst for the County Borough of Hull (Kingston-upon-Hull), in addition to Arnold R. Tankard (December 29th, 1932).

Milk Products Sub-Committee's Report, No. 3

ERRATA

ANALYST, 1932, **57**, 650. Line 3 from bottom. Add to the reagents required: "2 *N* sodium hydroxide solution (approximate)."

(P. 651.) *For* "add *N*/2 sodium hydroxide solution" *read* "add the 2 *N* and, towards completion, *N*/2 sodium hydroxide solution."

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(From the beginning of the year 1921 to date)

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LOTHIAN and WARD. Action of Chlorinated Water on Galvanised-Iron Tanks. *J. Roy. Army Med. Corps*, 1922, **39**, 163; *J.S.C.I.*, 1923, 68A. (This water dissolves more zinc than untreated water.)

LOURIE. Report on Eggs and Egg Products. *J.A.O.A.C.*, 1922, **6**, 4; *C.A.*, 1923, 1512. (Method for zinc given.)

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PFYL and SAMTER. Alkalinity of the Ash of Foodstuffs. II. Experimental Groundwork. Simultaneous Titration of a Series of Ash Components. *Z. Nahr. Genussm.*, 1923, **46**, 241; *J.C.S., Abs.*, 1924, ii, 276. (Methods for zinc and lead given.)

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SALE and BADGER. Contamination of Beverages and other Foods with Zinc. *Ind. Eng. Chem.*, 1924, **16**, 164; ANALYST, 1924, **49**, 192. (The extents to which galvanised buckets are corroded by beverages are determined.)

SATO and MURATA. Determination of Zinc in Milk. *Trans. Tottori Soc. Agric. Sci.*, 1931, **2**, 206; *B.C.A.*, 1932, 638A. (Nephelometric as ferrocyanide.)

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SHOJI. Analysis of Liver Ash by means of the Polarograph. *Bull. Inst. Phys. Chem. Research, Tokyo*, 1931, **10**, 162; *C.A.*, 1931, 4293. (Data for zinc.)

SIMPSON. Minor Elements in Living Organisms. *Chem. Eng. Mining Rev.*, 1932, **24**, 323; *C.A.*, 1932, 4612. (Zinc and other elements referred to.)

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VAS. Solution of Zinc and Copper Plating by Milk and Whey. *Kixérlet. Közlem.*, 1923, **26**, No. 1–4, 1; *C.A.*, 1926, 2028.

VON DER HEIDE. Determination of Copper and Zinc in Wine. *Z. anal. Chem.*, 1925, **66**, 24; ANALYST, 1925, **50**, 296. (Both metals precipitated as sulphides and weighed as oxides.)

WOLFF. The Occurrence of Zinc in Oils from Animals and Plants. *Nederland. Tijdschr. Geneeskunde*, 1923, **67**, II, 399; *C.A.*, 1923, 3190. (When oxidised with nitric and sulphuric acids, but not when ashed, cod-liver oil shows zinc.)

WRIGHT and PAPISH. Inorganic Constituents of Milk. *Science*, 1929, **69**, 78; *B.C.A.*, 1929, 953A. (Spectrographic examination reveals a number of metals, including zinc.)

ZBINDEN. The Infinitely Small Quantities of Certain Elements in Milk and their Detection by the Spectrographic Method. *Lait*, 1931, **11**, 114; *C.A.*, 1931, 4032.

T. H. P.

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1932

FORTY-ONE of the 1206 samples submitted under the Food and Drugs Act were bought formally and 1165 informally. Thirty-six (23 of which were milks) were returned as incorrect.

IMITATION ALE AND BEER.—These samples were contained in bottles similar to those used for a well-known proprietary brand of beer and ale, and the labels, which were also printed in imitation of the same articles, described them respectively as "Special Lager Mild Ale" and "Black Malt Beer." The percentages of proof spirit present were, respectively, only 2·2 and 2·4 per cent., so that, practically speaking, they were non-alcoholic drinks. According to the Finance Act, 1932, liquor must not be described by any name calculated to indicate that the substance is ale or beer unless duty has been paid, and the bottlers were cautioned.

"HOME-MADE" LEMON CURD.—The description "Home-made" lemon curd indicates a fairly definite composition, *i.e.* containing butter, sugar, eggs and lemon only. This sample contained only 3 per cent. of fat, which was margarine, and 5 per cent. of eggs, together with about 8 per cent. of flour which, presumably, was used for the purpose of thickening. There was also an excess of water present, after allowing for the amount contained in the constituents, of about 10 per cent., and there was, also, no evidence of the presence of lemon rind. Altogether it was a most unsatisfactory article masquerading under a description which is used to denote a first-class one. The vendor was cautioned.

H. H. BAGNALL

CITY OF GIBRALTAR

REPORT OF THE CITY ANALYST FOR THE YEAR 1931

THE total number of specimens and samples of all classes examined during the year 1931 was 4519. Over ninety-eight per cent. of the work was in connection with the public health of Gibraltar and the personal well-being of the people.

It is satisfactory to be able to report a marked reduction in the number of foodstuffs found to be below the statutory limits. For the greater part the defects were not of a serious nature. An increase of ninety-five samples taken under the Public Health Ordinance is noticed. A series of bacteriological examinations were carried out as a check on the efficient sterilisation of milk.

GOATS' BOILED MILK.—It is satisfactory to report that no sample of imported goats' milk was found to be unboiled or to contain a proportion of unboiled milk.

Of the seventy-six samples of goats' milk analysed, six were found to be deficient in milk-fat as the result of skimming by the vendor. Milk samples deficient in fat the previous year amounted to 21 per cent., so that it would appear that the vendors are taking more care not to deprive this article of diet of its fat when clearing it of scum which is likely to form on the surface after boiling. No legal proceedings are taken when the vendor declares at the time of purchase that the milk has been skimmed. In my opinion the practice of robbing milk of its natural fat to such an extent that it contains less than the statutory limit is most unsatisfactory, and should be prohibited.

NITRATES IN GIBRALTAR DRINKING WATERS.—In investigating the nitrate test for adulterated milks under local conditions it was found that Gibraltar drinking waters, *i.e.* the general supply and tank waters of private houses contained no nitrates, but that all of the underground streams (Gibraltar) and drinking waters procured from La Linea and surrounding district contained them to a marked degree. Conclusions drawn, therefore, are (i) the nitrate test cannot be applied if milks are adulterated in Gibraltar; (ii) if water is added to milk before importation, it would be possible in the majority of cases to prove this by the presence of nitrates.

A. G. HOLBOROW

GOVERNMENT OF MADRAS

REPORT OF THE PUBLIC ANALYST FOR THE YEAR ENDING SEPTEMBER, 1931

OF the 2091 samples examined, 1777 were submitted under the Prevention of Adulteration Act, and 310 were miscellaneous food and drugs from Government hospitals and institutions. The tabulated results of analyses show the appalling extent to which dishonesty exists amongst food-vendors generally. Of the total number of samples taken, it will be seen that more than 40 per cent. were adulterated, whilst in the case of essential articles of food such as ghee and milk, more than 50 per cent. of the samples had to be condemned. In considering these figures it should be borne in mind that a sample-taker carrying out his duties labours under a number of special disadvantages, more particularly the fact that he is known and that, when he decides to devote a day to taking samples, information of his activities will spread rapidly. A second point on which comment is required is the total inadequacy of the fines inflicted. The average fine is only Rs. 9 for all samples, and in only one municipality does it exceed Rs. 20. I believe that in many cases hawkers or petty vendors have been prosecuted. Even in such cases the least fine that should be inflicted for a first conviction, with any probability of its causing a definite check to food adulteration, is Rs. 20. During the year the highest fine imposed was Rs. 75 in Coimbatore in connection with one of the worst cases of adulterated milk within my experience. This was sold as genuine buffalo milk—a milk normally very rich in cream. When analysed it was found to consist of approximately equal proportions of separated (machine-skimmed) milk and water.

Of the 267 samples of tea examined, 72 were adulterated. It is unfortunate that no prosecutions were instituted in the Virudhunagar district, which is a big distributing centre for adulterated tea.

When the further extension of the Act, which is now contemplated, is made, the local bodies concerned should be told that their contribution should not be considered an unavoidable expense, but should rather be regarded as a penalty to which they will have to submit in the event of their not taking full advantage of the facilities given them by Government and partly maintained out of their contribution. With proper working of the Act, large as well as small vendors

being sampled and proper production of cases before the Magistrates, I have little doubt that the fines realised would more than cover the municipal contributions.

There have been two appeals to the High Court from convictions obtained under the Prevention of Adulteration Act. The grounds of appeal in both cases involved technical points connected with the regulations made under the Act. In one case a ghee merchant (Madras City), who had been convicted of selling ghee containing a large proportion of foreign fat, was successful in his appeal. In another case the conviction of a dealer (Kumbakonam), who sold "French Coffee" which was found to contain chicory was upheld. New regulations which, it is hoped, will be less liable to misconstruction have been drafted, and will, it is anticipated, be officially adopted in the very near future.

TEA ADULTERANTS.—The usual adulterant found was blackgram husk, but in two cases there were 10 and 60 per cent. of an unidentified imitation tea-leaf.

COFFEE ADULTERANTS.—In Madras City 93 samples of coffee were certified as adulterated, and 64 vendors were prosecuted. The usual adulterants was chicory or exhausted coffee. One sample, from Virudhunagar, contained 40 per cent. of imitation coffee, probably a preparation of tamarind seed. Another consisted of a mixture of 25 per cent. of coffee, 25 per cent. of a wheat flour preparation, and 50 per cent. of exhausted coffee and chicory.

HERBERT HAWLEY

Report of the Government Chemist upon the Work of the Government Laboratory

FOR THE YEAR ENDING 31ST MARCH, 1932*

IN addition to doing work for the same Government Departments as last year (ANALYST, 1931, **56**, 809), members of the Government Laboratory have been seconded during the year 1931–1932 for work in connection with river surveys carried out by the Ministry of Agriculture and Fisheries for the Water Pollution Board, and for the Medical Research Council. The total number of samples examined during the year in the Laboratory, including those dealt with at the Chemical Stations, was 473,055, showing a decrease of 44,407 as compared with the previous year, which, in its turn, showed a decrease of 27,960 on 1930, reflecting the present state of industry. Upwards of 800 samples were submitted in connection with the Abnormal Importations Duty and General Ad Valorem Duty, both imposed during the year.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter and Margarine.*—Of 863 samples of butter and 349 of margarine, 4 butters and 5 margarines contained over 16 per cent. of water.

Cheese.—The general standard for fat was rather lower than for the previous year, but for *Cream* it was higher.

Sheep Dips.—Of 56 samples, 17 were reported as defective.

Fertilisers and Feeding Stuffs Act, 1926.—Of the 8 fertilisers submitted, 2 of the 5 mixed fertilisers contained less than one-fifth, and another less than one-third of the declared amount of potash, together with deficiencies in other ingredients. The 7 feeding stuffs included biscuit and meat meal, meat and bone meals, ground oats, pea meal and balanced rations. Excessive deficiencies in oil or protein, or both, were found in the biscuit and meat meal, in 2 meat and bone meals, and in the balanced rations. Ground oats contained 17 per cent. of barley, and the pea

* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 9d. net.

meal an excessive proportion of pea-seed husk. The results confirmed those of the Agricultural Analysts in all cases but one.

Agricultural Produce (Grading and Marking) Act.—Two-hundred-and-sixteen plain flours, 120 self-raising, and 156 Yeoman flours, and 5 samples of wheat and 27 of wheatmeal were tested; 377 samples of cider and 4 of cider constituents were examined under the National Mark Scheme, and a commercial preparation recommended for use in National Mark Cider was found to be a solution of phosphoric acid.

Miscellaneous Articles.—Two samples of honey were examined, and tests were applied to a series of glass specific-gravity beads in connection with the projected standard for specific gravity in National Mark honey.

CUSTOMS AND EXCISE.—*Beer.*—The total number of samples was 48,055—a decrease of 4368 on the previous year, and most of these were examined to determine the original gravity. Of the 1930 samples of beer as retailed, there was evidence of dilution in 184 cases, and in 15 cases the dilution was equivalent to the addition of over 4 gallons of water per barrel. The examination of 1987 samples of beer and brewing materials for arsenic showed that it was present in slight excess of one-hundredth of a grain of arsenious oxide per pound or per gallon in 64 cases.

Cocoa and Chocolate.—To assess duty and drawback, 13,429 samples were examined, 9411 from imported and 4003 from exported goods.

Hydrocarbon Oils Duty.—Of 10,031 samples examined, 7807 were from imported and 2224 from exported goods, and, of these, 6217 consisted of hydrocarbon oils and 3814 of miscellaneous composite goods such as enamels, varnishes, road dressings.

Hydrometers, Saccharometers and Thermometers and Graduated Vessels.—Tests were made on 2059 pieces of apparatus. The "A" hydrometers in use for revenue purposes are being gradually converted into "B" instruments.

Abnormal Importations (Custom Duties) Act, 1931, and Import Duties Act, 1932.—Sixty-eight samples were examined in order to determine whether they came under the scope of the free lists, and 785 for their liability under various categories. A large proportion consisted of samples of fabrics, felts, fibres, yarns, cordage, braid, leather cloths, minerals, ores, cosmetics, and toilet requisites.

Spirits.—During the year, 13,594 samples of exported medicinal spirits, tinctures, liniments, etc., were examined, and in 160 cases the declared strength of the spirit was over-stated. Of imported spirits and spirituous preparations 10,606 samples were tested.

Sugar.—For assessment of duty or drawback 71,912 samples of sugar were examined; 816 of glucose for assessment on exportation; 192 samples of imported materials were searched for *Saccharin*, and 396 samples of saccharin containing other substances were examined to ascertain the amount of drawback payable.

Tea.—Of 26,756 samples, 124 (representing 746 packages) were reported against, 87 on account of the presence of foreign substances and 37 as unfit for human consumption.

Tobacco.—Of imported unmanufactured tobaccos, 13 of 121 samples contained non-permissible substances, and 187 of 274 samples of imported manufactured tobacco, cigarettes, and snuff submitted for classification contained ingredients not allowed to be used for tobacco in this country. The percentage of moisture in tobacco for home consumption was determined in 8626 samples, and oil in 841 samples. Moisture, inorganic matter, sand and extraneous matter were recorded in offal tobacco for export in 42,442 samples.

MINISTRY OF HEALTH.—Of the 130 condensed milks examined, 30 were reported against for wrong labelling, but in five cases the milk was below the minimum standard. The presence of preservatives was looked for in 1512 samples of imported dairy produce, and in 792 samples of other foodstuffs, and, of these, 21 samples contained sulphur dioxide and 5 benzoic acid, contrary to regulations. Two samples of butter contained boron preservative, but the quantity found in each case was so small as to render it unlikely that boric acid had been added for preservative purposes. Four samples of sugar-goods coated with metallic wrappings contained copper and zinc in proportions varying from 0·4 to 2·8 per cent.

FOOD AND DRUGS ACT.—Sixteen samples of food and one of medicine were examined during the year. The foods consisted of eleven samples of milk alleged to be deficient in fat or non-fatty solids, two samples of mince, and one each of jam alleged to contain excess of sulphur dioxide, sardines in olive oil, alleged to contain cotton-seed and no olive oil, and a cream containing foreign fat. The presence of cotton-seed in the oil from the sardines was not established. In thirteen cases the results were in agreement, and in two cases in disagreement with those put forward by the prosecution, and in two samples it was possible neither to determine the loss of sulphur dioxide during storage nor to state the proportion present in the sample when it was purchased. A sample of milk alleged to be deficient in fat contained 3·20 per cent.

D. G. H.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Detection of Small Quantities of Hexamethylene-tetramine in Fish-Preserving Pickle-Liquor. A. Van Druten. (*Chem. Weekblad*, 1932, **29**, 501–504.)—As a preliminary test, 10 (or 50 c.c.) of filtered liquor are steam-distilled with 1 to 3 c.c. of 85 per cent. phosphoric acid, and 5 c.c. of the distillate (which should amount to 25, or 250 c.c.) are tested for formaldehyde (*e.g.* by the author's method, *id.*, 1931, **28**, 283). If the test is positive, the presence of formaldehyde, as a decomposition-product of hexamethylene-tetramine (urotropine), is confirmed by observation under the microscope of the crystals formed on mixing 1 drop each of filtered sample and 5 per cent. mercuric chloride solution; hexamethylene-tetramine forms stars with three, four or six points, and they change eventually to octahedra at a rate which depends on the amounts of reactants present. As a final confirmation, solid calcium carbonate is added to 75 c.c. of the sample until no more carbon dioxide is evolved, and the liquid is then made just alkaline to litmus with solid calcium oxide and filtered. The filtrate (50 c.c.) is extracted for 2½ hours with chloroform, the extract is evaporated, and the resulting dry residue is extracted twice with cold water. The filtrate from this extraction is also evaporated, and the new residue is tested with mercuric chloride (*vide supra*) after addition of 1 drop of 0·1 *N* hydrochloric acid. The test is sensitive to 0·5 mgrm. of hexamethylene-tetramine in 50 c.c. of pickle, although for pure solutions in water the maximum sensitiveness attainable is 1:500,000.

The rate of decomposition of hexamethylene-tetramine into formaldehyde and ammonia is dependent to some extent on the p_H value. The decomposition-reaction is reversed in alkaline solution (*cf.* the above test), and at room-temperatures decomposition is complete after 13 and 30 days in mixtures of 0·05 per cent. of hexamethylene-tetramine (the amount usually taken for preservation) with 4 per cent. of common salt in 5 and 2 per cent. acetic acid, respectively. Sodium or potassium hydroxide is not recommended as neutralising reagent, since the resulting acetates are soluble in chloroform. The decomposition of the hexamethylene-tetramine usually occurs more rapidly than the disappearance of formaldehyde from the pickle liquor (*cf.* Behre and Ulex, *Z. Unters. Lebensm.*, **1931, 62,** 58). J. G.

[Determination of] Citric Acid in Milk. B. G. Hartmann and F. Hillig. (*J. Assoc. Off. Agr. Chem.*, 1932, **15**, 643–645.)—The method described is based on the conversion of the citric acid into pentabromoacetone. To 50 grms. of milk, or 6 grms. of dried milk plus 44 c.c. of water, in a 150 c.c. beaker, about 0·1 grm. of tartaric acid and 6 c.c. of *N* sulphuric acid are added. The beaker is placed on a steam-bath for 15 minutes, after which 3 c.c. of 20 per cent. phosphotungstic acid solution are stirred in and the heating continued for 5 minutes. The liquid is then transferred to a 250-c.c. measuring flask with 95 per cent. alcohol, cooled and made up to volume with the alcohol, and filtered through a pleated filter-paper. Two hundred c.c. of the clear filtrate, transferred to a 16-oz. centrifuge bottle, are shaken vigorously for 2 minutes with 10 c.c. of lead acetate solution (75 grms. of crystals and 1 c.c. of glacial acetic acid, made up to 250 c.c.) and centrifuged for 15 minutes at about 900 r.p.m. If a little of the supernatant liquid gives a precipitate with the lead acetate solution, it is returned to the bottle with more of the acetate solution and again shaken and centrifuged. The speed and duration of centrifuging must be increased if the sediment lifts. The bottle is left inverted for several minutes to drain, the precipitated salts being then transferred to a 400-c.c. beaker with about 150 c.c. of water. The liquid is warmed, treated with a rapid stream of hydrogen sulphide, with frequent stirring, until cool, made up to 250 c.c. in a measuring flask with water, and filtered through a folded paper. In a 500-c.c. Erlenmeyer flask containing a few small glass beads, 200 c.c. of the filtrate are evaporated to about 75 c.c., the residue being cooled, mixed with 10 c.c. of dilute sulphuric acid (1 : 1) and 5 c.c. of potassium bromide solution (15 grms. in 40 c.c. of water), heated at 48° to 50° C. for 5 minutes, and at once treated with 20 c.c. of potassium permanganate solution (5 grms. in 100 c.c.). The stoppered flask is shaken vigorously for about a minute, with frequent release of the pressure, and then left for 4 minutes, the temperature being kept below 55° C. meanwhile. If no precipitation of manganese dioxide occurs, the determination must be started again with a larger amount of the permanganate solution. The dioxide is destroyed by addition of a solution containing 40 grms. of ferrous sulphate and 1 c.c. of sulphuric acid per 100 c.c. of water (20 c.c. usually suffices), the mixture being cooled in ice-water, shaken well until the pentabromoacetone is precipitated in the crystalline form, and left in a refrigerator overnight. The solution is then filtered rapidly, by decantation, through a thin, tight asbestos pad

on a Gooch crucible. The volume of the filtrate (S. c.c.) is measured and the filtrate is used to transfer the precipitate to the crucible, the contents of which are washed at once with 50 c.c. of ice-cold water. The crucible is dried either in a vacuum over sulphuric acid or by aspiration with air, and weighed. After removal of the precipitate with three successive 20 c.c.-portions of alcohol, followed by three of ether, the crucible is again dried and weighed, the loss in weight (P grms.) representing pentabromoacetone. The weight in grams of the citric acid in the portion taken for analysis is given by 1·64 (0·424 P + 0·000017 S).

With a synthetic milk prepared from calcium caseinate, lactalbumin, lactose, butter-fat, and sodium phosphate, and containing known proportions of citric acid added as calcium salt, satisfactory results were obtained. Five bottled milks showed, respectively, 0·163, 0·168, 0·171, 0·172, and 0·177 grm. of citric acid per 100 c.c., and a dried whole milk 1·32 grm. (0·173 when reconstituted).

T. H. P.

Potentiometric Titration of Strongly Coloured Fruit Solutions containing added Phosphoric Acid. A. Gaines, Jr. (*J. Assoc. Off. Agr. Chem.*, 1932, **15**, 617–618.)—Highly-coloured fruit solutions are often not satisfactorily decolorised by the treatment with lead acetate recommended by Hartmann and Hillig (ANALYST, 1930, **55**, 517); in some cases the natural colouring matter is too concentrated to be affected appreciably, and in others artificial colour is present. It has been shown that potentiometric titration is applicable when natural colouring matters are the only interfering substances present in the fruit solution. With artificially-coloured solutions, direct potentiometric titration of the diluted liquid is suitable, as none of the permitted water-soluble coal-tar dyes interferes in the titration. When added phosphoric acid is present, the lead acetate method may be used, and experiments with solutions of citric, malic, and tartaric acids, each containing phosphoric acid, show that potentiometric titration of the lead-free filtrates gives satisfactory results, in agreement with those of Hartmann and Hillig's method. The quinhydrone electrode is preferable to the hydrogen electrode, as it is simpler to use and reaches equilibrium the more rapidly. T. H. P.

Determination of Iron in Cow's Milk and Human Milk. F. Reis and H. H. Chakmakjian. (*J. Biol. Chem.*, 1932, **98**, 237–240.)—The method previously described by Reis and Chakmakjian (*J. Biol. Chem.*, 1931, **92**, 59) for the determination of iron in blood as dispersed Prussian blue has been applied to the analysis of milk. The same solutions are needed, but for a more reliable standard ferric sulphate solution, 7·0226 grms. of ferrous ammonium sulphate ("C.P.") are dissolved in about 50 c.c. of water and 10 c.c. of concentrated sulphuric acid. The hot, nearly boiling, solution requires about 18 c.c. of 0·2 *N* potassium permanganate solution for oxidation to the ferric state. The oxidised solution is cooled, transferred to a litre flask, diluted with the washings, and made up to volume. This stock solution contains 1 mgrm. of iron per c.c., and 10-fold dilution gives the standard solution. A Pyrex micro-Kjeldahl flask graduated on the neck to 10, 15 and 25 c.c. is the digestion tube used. To 5 c.c. of milk in a digestion tube 1 c.c. of concentrated sulphuric acid is added, and the uppermost part of the liquid

is heated carefully to prevent loss. When dense acid fumes appear, 1 c.c. of fresh acid is added, the whole is heated for a minute, and 2 c.c. of saturated potassium chlorate solution are slowly added. The liquid is heated for 3 minutes, and 1 c.c. of potassium chlorate solution is added, drop by drop. After vigorous heating of the mixture for 2 minutes, the addition of chlorate, 1 c.c. at a time, is continued, and the liquid is heated each time for 2 minutes, until its colour is brown. A small funnel in the stem of the digestion-tube serves as a condenser for the acid fumes, and a larger funnel inverted over the small one removes uncondensed fumes by suction. A small drop of 0·2 *N* permanganate solution, followed by 1 c.c. of concentrated sulphuric acid and 1 c.c. of potassium chlorate solution, are added, then more chlorate, until the colour of permanganate reappears for a few seconds, when most of the organic matter is destroyed. To ensure complete oxidation, 2 c.c. of water, 4 or 5 drops of 10 per cent. glucose or sucrose solution, and 1 c.c. of chlorate solution are added slowly; the liquid is heated until dense fumes of acid are produced, and gentle boiling is continued for 5 minutes, or until the residual thick liquid is clear; it may require about 15 c.c. of chlorate solution. The liquid is cooled and diluted to about 5 c.c., and, if the solution is clear, 0·2 c.c. of gum ghatti and potassium ferrocyanide solution is added, and the whole is diluted to the 10-c.c. mark. The standard solution is prepared in a 50-c.c. flask; to 1 c.c. of standard iron solution are added 2 c.c. of concentrated sulphuric acid, 2 c.c. of a 10 per cent. solution of ammonium sulphate to compensate the ammonium salt obtained from the milk, and 10 to 15 c.c. of 6 per cent. potassium sulphate; the solution is cooled, 1 c.c. of gum ghatti and potassium ferrocyanide solution is added, the whole is mixed, and then diluted to the 50-c.c. mark. Both solutions are well shaken for a few minutes, left for 15 minutes, and then compared. *Calculation Example.*—The digestion product from 10 c.c. of milk was converted into 15 c.c. of Prussian blue solution; the standard was diluted to 50 c.c. With the standard set at 20, the reading of the unknown was 17·5, the ratio of dilution being 0·3. $\frac{20\times0\cdot1\times0\cdot3}{17\cdot5} = 0\cdot0343$ mgrm. of iron in 10 c.c. of milk, *i.e.* 0·34 mgrm. in 100 c.c., but actually 0·32 mgrm. after subtracting the amount of iron found in the reagent used. Apparently a small part of iron in milk owes its origin to rusty cans. P. H. P.

Determination of *l*-Malic Acid in Fruits and Fruit Products. B. G. Hartmann and F. Hillig. (*J. Assoc. Off. Agr. Chem.*, 1932, **15**, 645–653.)—The polarimetric determination of malic acid in fruit-products involves the preliminary removal of pectin, sugars, tartaric acid, etc. Not only does pectin tend to give colloidal solutions, and thus impede filtration, but its fundamental constituent, pectic acid, is strongly dextrorotatory. Treatment with strong alcohol precipitates the main portion of the pectin, the last traces of which may be subsequently removed by means of tribasic lead acetate. For eliminating the sugars the alcoholic filtrate from the pectin precipitation is treated with lead acetate solution, the malic and certain other organic acids being precipitated quantitatively, whilst the sugars pass into solution. Besides sugars, lead acetate treatment removes the monobasic acids—lactic, glycollic, benzoic, salicylic, and quinic—all of which may

be present in fruit-products, either normally or added. Sugars are only sparingly soluble in 80 per cent. alcohol, so that three additional washings with the alcohol are necessary.

The lead precipitate may contain malic, citric, isocitric, tartaric and succinic acids, and tannins, all of which, except citric and succinic acids, are optically active. Tartaric acid is only partially removed by precipitation with tribasic lead acetate, but in the form of cream of tartar the acid is practically insoluble under the conditions employed. It is not necessary to permit the reaction mixture to stand overnight in a refrigerator to complete the precipitation, vigorous shaking with glass beads for 10 minutes, before and after 30 minutes' rest in the refrigerator, being equally effective. The high concentration of alcohol used causes a small loss of malic acid, owing to occlusion of acid potassium malate in the cream of tartar precipitate; this and other errors are corrected by using an empirical factor in the final calculation. The addition of tartaric acid to the sample to be analysed not only hastens, but also renders complete, the precipitation of cream of tartar. Citric and isocitric acids, tannins, and colouring matters are removed by tribasic lead acetate.

Free malic acid is not precipitated by normal lead acetate; its lead salt remains dissolved in the liberated acetic acid, and those of fruit acids generally are increasingly soluble in excess of acetic acid and of lead acetate. It is, however, found that careful control of the amounts of the acid and acetate leads to a percentage recovery of malic acid which is practically constant for solutions of widely varying composition. To prepare the tribasic lead acetate a modified form of Payen's procedure (*Ann. Chim. Phys.*, 1866, [4], **8**, 303) is used and, as the salt slowly hydrolyses in aqueous solution, freshly-prepared solution must be used. With this solution, the permitted coal-tar colouring matters form lakes which are almost completely decolorised by hydrogen sulphide. The final pure malic acid solution is evaporated to small volume, neutralised with alkali, made slightly acid with acetic acid, saturated with uranium acetate, and polarised. Full details of the procedure are given.

The results obtained with a number of solutions containing various acids and sugars are mostly nearly theoretical, and never show a greater error than 3 per cent. The percentages of *l*-malic acid in a number of fruit and fruit-products are given, these varying from 0·03 in blackberry jam to 0·49 in canned peaches, and 0·50 in damson plum jam. T. H. P.

Further Studies on the Wax-like Coating of Apples. K. S. Markley, S. B. Hendricks and C. E. Sando. (*J. Biol. Chem.*, 1932, **98**, 103–107.)—Sando (*J. Biol. Chem.*, 1923, **56**, 457; ANALYST, 1923, **48**, 496) isolated from the petroleum spirit extract of Ben Davis apple peels, a paraffin hydrocarbon and a secondary alcohol, which were assumed to be triacontane, $C_{30}H_{62}$, and 14-heptacosanol, respectively. Channon and Chibnall (*Biochem. J.*, 1929, **23**, 186) reported the isolation of *n*-nonacosane and di-*n*-tetradecyl ketone from cabbage leaves, and suggested that the hydrocarbon isolated by Sando may have been *n*-nonacosane contaminated by the corresponding or a similar ketone. These products were identified with the aid of *X*-ray diffraction from the plane of greatest

spacing, a more trustworthy method which was not available to Sando in 1923. A re-investigation of the petroleum spirit extract of the wax-like coating of apples directed particularly toward the isolation of a ketone has now been made by the authors, and has led to the following conclusions: The petroleum spirit extract of apple cuticle does not contain a ketone in quantities which can be isolated. The principal hydrocarbon, constituting the bulk of the petroleum spirit extract, is *n*-nonacosane, m.pt. 65·1° C., and not triacontane as previously reported. The secondary alcohol is 10-nonacosanol, and not 14-heptacosanol, although both alcohols have the same melting-points, as do also their corresponding acetates. The peel from Rome Beauty apples and Ben Davis apples was examined. Coincident with the completion of this work, Chibnall and his associates (*Biochem. J.*, 1931, **25**, 2095; ANALYST, 1932, **57**, 258) described a thorough examination of the petroleum spirit extract of apple peels, which had led to substantially the same results as this investigation. In no case have the authors observed the melting-point of what they consider a pure sample of nonacosane to be as low as that reported by Chibnall and his co-workers. P. H. P.

Detection of Diacetyl in Fats to which Butter Flavours have been added. Azern and Guillot. (*Ann. Falsificat.*, 1932, **25**, 459–462.)—Fifty grms. of the fat (made up to contain about 0·1 grm. of flavour per kilo, or 0·02 grm. of diacetyl) and 20 c.c. of 95 per cent. alcohol are shaken together, and 20 c.c. of the mixture are rapidly distilled by placing the flask in a calcium chloride bath boiling between 115° C. and 120° C. The distillate and 5 c.c. of water washings of the receiver are treated by addition of 1 c.c. of hydroxylamine hydrochloride, 1·7 c.c. of a *N* solution of sodium hydroxide, and after shaking for 1 minute, 1 c.c. of a 1 per cent. solution of nickel sulphate and 0·6 c.c. of *N* acetic acid are added, drop by drop, while still shaking. The alcohol is evaporated, and when only 2 to 3 c.c. of liquid remain, a red zone adhering to the wall of the dish is characteristic of dimethylglyoxime. Butter itself does not give a positive reaction, this appearing to indicate that its characteristic flavour is not due to diacetyl. D. G. H.

Composition of Illipè Butter. G. Schuster. (*J. Pharm. Chim.*, 1932, **124**, 421–431.)—The two samples of illipè butter examined had the following characteristics:—Saponification value, 199·7, 199·4; iodine value, 47·64, 46·82; unsaponifiable matter, 2·1, 2·4 per cent.; acid value (as stearic acid), 4·63, 1·8; ash, 0·5, 0·3 per cent. The fats were oxidised with permanganate in acetone solution, and from the results the glycerides were calculated to have the following composition: Fully-saturated, 6·78 (tristearin 1·4; palmitodistearin, 5·2); di-saturated mono-ethylenic, expressed as oleic esters, 61·5 (dilauric-β-olein, 21·3; distearic-β-olein, 40·2); mono-saturated diethylenic expressed as oleic esters, 8·9 (β-monostearic-α-α-olein, 5·4; β-palmitic-α-α-olein, 3·5); triethylenic glycerides, 12·22 (triolein). During the course of the work certain new synthetic azelaic glycerides were prepared which served to identify the azelaic glycerides obtained on the oxidation of illipè butter; α-α-distearic β-azelain, m.pt. 67° C.; β-stearic α-α-diazelain, m.pt. 61° C.; β-palmitic α-α-diazelain, m.pt. 57° C.; also α-α-distearic

β-palmitin, analogous to the product prepared by Amberger and Wieshaln, m.pt. 63° C. α-α-Dilauro-β-azelain can be partly saponified to form α-α-dilaurin, melting at 22°–23° C. D. G. H.

Distinction between Lecithin Preparations of Animal and Vegetable Origin. F. E. Nottbohm and F. Mayer. (*Chem.-Ztg.*, 1932, **56**, 881–882.)—Juckenack's method of detecting lecithin consists in extracting the de-fatted substance with hot alcohol and determining the phosphorus-content of the extract, the assumption being made that the phosphorus is derived solely from lecithin. This may be approximately true for animal lecithins, but is certainly not so for those of vegetable origin (*cf.* ANALYST, 1932, **57**, 322). Since choline is an essential constituent of egg-yolk lecithin, determinations have been made of the choline in samples of commercial lecithins prepared from egg-yolk and from soya beans. One grm. of the material was heated with 10 c.c. of hydrochloric acid (sp.gr. 1·124) and 50 c.c. of water in an autoclave under 4·5 atmospheres pressure. The separated fatty acids were thoroughly washed with hot water, and the aqueous solution was boiled with animal charcoal and filtered. The filtrate was made up to 100 c.c., and 20 c.c. (cooled in ice) were mixed in a thick-walled centrifuge tube of about 30 c.c. capacity, with 6 c.c. of strong iodine solution (*loc. cit.*, and Roman, *Biochem. Z.*, 1930, **219**, 218), and left for about 15 minutes in ice-water before centrifuging. The supernatant liquid was poured through an Allihn filter-tube containing asbestos, and the precipitate of choline ennea-iodide was washed with about 10 c.c. of water in small portions, and afterwards dissolved in alcohol and titrated with 0·1 *N* thiosulphate solution.

Various samples of lecithin have been examined, the percentage of lecithin present being calculated from (1) the choline, as determined as above, (2) the phosphorus-content and (3) the nitrogen-content. The results are as follows:—Lecithin Kahlbaum *ex ovo*, (1) 60·02, (2) 76·60, (3) 97·41. Lecithin Merck *ex ovo puriss.*, (1) 70·41, (2) 98·00, (3) 116·58. Three samples from soya beans: (*a*) (1) 13·20, (2) 51·04, (3) 42·55; (*b*) (1) 16·28, (2) 59·40, (3) 47·43; (*c*) (1) 21·08, (2) 72·20, (3) 57·35. Lecisan (also from soya beans) (1) 15·82, (2) 72·40, (3) 58·22.

With pure lecithin the ratio N : P should be 1 : 1, but the commercial egg-products gave the values 1 : 0·79 and 1 : 0·84 for this ratio, and the soya-bean products values varying from 1 : 1·20 to 1 : 1·25. The difference in composition between the products of the two classes is shown more clearly if the total nitrogen- and phosphorus-contents are diminished by the amounts derived from the choline determination. The ratio (residual N) : (residual P) then becomes 0·44 and 0·69 for the two egg-yolk products, and 1·29 to 1·33 for the soya-bean products.

Lecithins of both types contain non-lecithin material, those from egg-yolk showing 60 to 70 per cent. of lecithin and those from soya beans only 13 to 21 per cent., or, calculated on the oil-free material, 20 to 26 per cent. Moreover, indications are obtained which suggest that plant lecithins are phosphatid-like substances differing in structure from egg lecithins. The authors emphasise the inadvisability of using plant lecithins indiscriminately in place of the egg-yolk preparations in food products. T. H. P.

Colour Reactions of Different Varieties of Strophanthus Seeds with Sulphuric Acid. M. Wagenaar. (*Pharm. Weekblad*, 1932, **69**, 1340–1349.)—The literature of the subject is summarised with particular reference to the vexed question of the correct strength of the sulphuric acid (*cf.* especially, *id.*, 1928, **65**, 140, 164, 166, and 205), and a mixture of 3 parts of concentrated acid and 1 of glycerol is recommended as being more stable than the usual 80 per cent. acid, and as giving a colour which is more permanent, intense and selective. An intense green colour is normally produced with *Strophanthus Kombe*, whilst this reaction is less pronounced with *S. hispidus*, and seldom occurs with *S. gratus*. These differences may be related to the predominance of amorphous over crystalline glucoside in *S. kombe*, the reverse being the case in *S. gratus*. The colour is first apparent in the endosperm, particularly in the marginal cells, and then spreads to the outer cells of the cotyledon, and eventually throughout the whole structure; it is readily soluble in the oleo-plasma of the seeds. A mixture of equal volumes of a 10 per cent. solution of sodium hydroxide or of ammonia with glycerol may also be used, and produces an intense yellow in cells containing glucosides. These reactions are probably a measure of the quantities of cymarigin glucoside or fructoside (in the case of *S. kombe* and *hispidus*) or of cymarigenin rhamnoside, the colour being produced by condensation of cymarin with hydroxymethyl furfuraldehyde (from the dextrose or fructose) or with methyl furfuraldehyde (from rhamnose), respectively, with sulphuric acid as condensing agent (*cf.* Jacobs and Hoffmann, ANALYST, 1928, **53**, 660). The exact shade of the colour is probably influenced by the nature of the sugars present; and in the case of the sulphuric acid reagent it changes from green to red or violet on warming. J. G.

Application of Adsorbing Agents to the Removal of Poisonous Matters from Tobacco Smoke. A. Schaarschmidt. (*Chem.-Ztg.*, 1932, **56**, 911–913.)—Cigars, 12 cm. long and weighing about 9 grms., were smoked automatically in 50 minutes, except for a residual stump of 2·4 grms.; cigarettes were smoked in 7 minutes. The resulting gases were analysed before and after purification by the absorbing agent by passage in succession through two U-tubes containing cotton-wool soaked in 10 per cent. sulphuric acid, and a wash-bottle fitted with a sintered glass disc, and also containing the acid. The combined acid solutions were then made alkaline with sodium hydroxide solution and the mixture was steam-distilled into 80 c.c. of acetic acid until a volume of 2 litres of distillate was obtained (*A*). Of this, 400 c.c. were again made alkaline and steam-distilled, the first litre being received in a flask containing 50 c.c. of 0·1 *N* sulphuric acid, the excess of which was then determined by titration with 0·1 *N* sodium hydroxide solution with acid carmine as indicator, and the amount consumed was calculated as total volatile alkalinity. The second and third litres of distillate were titrated directly with acid, and the remaining 1600 c.c. of *A* were steam-distilled in the presence of 100 c.c. of glacial acetic acid, into 20 c.c. of 0·1 *N* sulphuric acid. When the total volume of distillate was 1·5 litre, the acid was back-titrated as before, and the result was calculated as pyridine. The residue from this distillation contained nicotine, which was precipitated after addition of a further 50 c.c. of glacial acetic acid in a volume of 250 c.c. with potassium bismuth iodide. The precipitate was removed

by filtration, shaken well with a mixture of 10 c.c. of 20 per cent. potassium hydroxide solution, 60 c.c. of ether and 60 c.c. of petroleum spirit for 30 minutes the non-aqueous layer was then removed, and the nicotine in 80 c.c. was titrated in the presence of 20 c.c. of 50 per cent. alcohol with iodo-eosin as indicator. Ammonia was calculated by deducting the sum of the nicotine and pyridine from the total alkali. Mean values for 4 cigars were 47·6 mgrms. of nicotine, 3·3 of pyridine, and 43·4 of ammonia. Activated charcoal (1 grm.) normally removed most of the nicotine and pyridine and some of the ammonia (*cf.* following abstract), but the rate of smoking is an important factor, since the temperature of the smoke is dependent on it. Gradual temperature-rises of 20° to 35° C. above room temperature during a smoking-period of 50 minutes were recorded. J. G.

Investigations on Tobacco Smoke. E. Waser and M. Stähli. (*Z. Unters. Lebensm.*, 1932, **64**, 470–485.)—Methods for the determination of nicotine in tobacco and tobacco-smoke are reviewed. The removal of nicotine from tobacco by steam-distillation with magnesium oxide, as in Pfyl and Schmitt's method (ANALYST, 1927, **52**, 728), is slow, and its completion is indicated by the absence of an opalescence on addition of 1 drop of a 12 per cent. solution of silicotungstic acid to 15 c.c. of distillate and 3 c.c. of 1 per cent. hydrochloric acid. Rasmussen's method (ANALYST, 1916, **41**, 208) is modified as follows:—The chopped sample (10 grms.) is shaken with 150 c.c. of water and 50 grms. of sodium chloride, and the mixture is steam-distilled with 10 grms. of anhydrous potassium carbonate, so that at the end of 1 hour it contains as little water as possible. The distillate, which is received in 3 c.c. of concentrated hydrochloric acid, is diluted to 500 c.c., and 100 c.c. are precipitated with 10 c.c. of the silicotungstic acid reagent, the precipitate being filtered on the following day and washed 8 times with 1 per cent. hydrochloric acid and weighed after 1 hour at 120° C. This method was shown to give results slightly higher than those obtained by Pfyl and Schmitt's method, the maximum deviations (0·03 per cent.) being obtained for tobaccos of high nicotine-content; they are probably due to the incomplete removal of the nicotine (*vide supra*). The m.pt. (with decomposition) of the nicotine dipicrate precipitated from a solution in benzene and recrystallised from ethyl alcohol was 222·0 to 222·5° C. (corr.). Pfyl and Schmitt's apparatus for artificial smoking (*loc. cit.*) was used to smoke 53 (out of a total of 68) mm. of a cigarette in 8 minutes, "pulls" of 4 seconds' duration being used. Addition of water to tobacco (nicotine-content, normally 1·3 per cent.) produced a progressive increase in the amount of nicotine removed in the smoke, the maximum being 16·2 per cent. of the total present for a moisture-content of 19 per cent. Bonicot's fluid (a solution containing a variable amount of tartaric acid and 1·2 per cent. of ferrous ammonium sulphate in 3·5 per cent. alcohol, *cf.* ANALYST, 1932, **57**, 727) was the most effective of the commercial fluid denicotinising agents examined, but it removed only 12 per cent. of the nicotine from the same tobacco, the moisture-content then being 13 per cent.; other preparations containing mainly water ("nicoton" and "supernic") had no more effect than could be explained by the water-content. Active charcoal (37·5 grms. or more) was shown to remove 80 to 94 per cent. of the nicotine from 500 c.c. of a 0·5 per cent. solution

on shaking for 15 minutes, but after re-activation of the carbon by successive extractions with 8 per cent. hydrochloric acid these values fell to 27 and 53 per cent. The condensates from cigar and cigarette tobaccos can be completely freed from nicotine by the action of active charcoal, and the extraction proceeds with much more rapidity and with less charcoal with cigars. Under the above conditions the maximum amount of nicotine (95 per cent.) removed from nicotine solutions is obtained by the action of 75 grms. or more of powdered silica gel, and most of the adsorption occurs during the first 5 minutes of contact; in this case also condensates from cigar tobaccos are the more easily treated. J. G.

Biochemical

Iron and Thorium Precipitation of Biological Fluids for Sugar and other Analyses. A. Steiner, F. Urban and E. S. West. (*J. Biol. Chem.*, **1932, 98**, 289–293.)—West, Scharles and Peterson (*J. Biol. Chem.*, 1929, **82**, 137) have used mercuric sulphate and barium carbonate precipitation in the preparation of blood filtrates for the determination of sugar by the Shaffer-Hartmann method. In this procedure the precipitating agents are removed with non-sugar constituents, and the filtrates are relatively free from added electrolytes. Owing to the time required for the preparation of filtrates, as well as the cost of mercuric sulphate, the method is not well suited to routine use, and attempts have been made for some years to find a metallic sulphate other than that of mercury which could be used with barium carbonate in a similar way, but would be free from these objections. Ferric sulphate and thorium sulphate have each been found suitable, and methods for the preparation of filtrates of blood plasma, spinal fluid and milk by precipitation with ferric sulphate and barium carbonate or thorium sulphate and barium carbonate, are described. Such filtrates are easily prepared, and give true sugar values in the Shaffer-Hartmann method, but they contain much more nitrogen than those prepared with mercury. Iron cannot be satisfactorily substituted for mercury in the treatment of urine and hydrolysed tissues. By the use of solid barium carbonate to neutralise the ferric sulphate, the p_H is automatically adjusted, both iron and sulphate are removed, and the filtrates give true sugar values without further treatment. All that is necessary is to use an excess of ferric sulphate. The filtrates may be used for the determination of creatinine and urea. Non-protein nitrogen values are about 25 per cent. lower than those found on tungstate filtrates. P. H. P.

Action of Copper in Iron Metabolism. C. A. Elvehjem and W. C. Sherman. (*J. Biol. Chem.*, 1932, **98**, 309–319.)—Recent work on the importance of copper as a supplement to iron for haemoglobin regeneration in anaemic rats is discussed. The authors present the results obtained when special emphasis was placed on the action of copper on the storage and utilisation of iron in the animal body. The liver and spleen are known to be storage centres for iron, and the authors have therefore investigated changes brought about in the iron-content of these

organs, when copper was added to the diet of anaemic animals and the iron thereby made available for haemoglobin formation. A chart shows the effect of post-natal care on the iron-content of young rats. The addition of pure iron to the milk diet of anaemic rats, which had been well depleted of their reserve of iron, had no effect on the haemoglobin content of the blood, but increased the total iron-content of the liver and spleen to a large extent. When the iron was replaced by copper, the store of iron in the liver was used directly for building blood haemoglobin. The copper caused only a slight decrease in the iron-content of the spleen, but produced a definite increase in the size of this organ. Further study is needed to elucidate the significance of this change. Inorganic iron (ferric chloride) was found to be much more readily assimilated and stored in the liver than organic iron (haematin). When graded quantities of inorganic iron were given by mouth to rats in the absence of copper, the haemoglobin-content of the blood remained unchanged, and the amount of iron stored in the liver was proportional to the amount of iron given. In the presence of copper, the rate of haemoglobin formation was dependent upon the iron intake, and the liver showed no iron storage until 0·3 mgrm. or more of iron was given daily. Therefore, when copper is present the inorganic iron is built directly into haemoglobin, and the amount in excess of what is needed for haemoglobin production is stored in the liver until the optimum level of iron storage in this organ is reached. It is impossible to increase the iron-content of rat livers much above 1 mgrm. per grm. of dry matter by prolonged feeding with iron either with or without copper. It is concluded that copper does not affect the assimilation of iron, but does play a part in the conversion of inorganic iron into haemoglobin. P. H. P.

Quantity and Composition of Milk obtained from Amputated Cow Udders. W. W. Swett, F. W. Miller and R. R. Graves. (*J. Agric. Res.*, 1932, **45**, 385–419.)—This investigation was made with the object of discovering the relationship between abundance of milk secretion and the internal and external characteristics of the udder. Eleven cows were killed, 4 in Group 1 by a blow on the head, 7 in Group 2 by shooting. The amputated udders of Group 2 were held at approximately blood temperature until after the second *post-mortem* milking. The average recovery was 61·1 per cent. for Group 1, and 75·32 for Group 2, and approximately 80 per cent. of the total milk recovered was obtained at the first *post-mortem* milking. The butter-fat of the milk obtained from the amputated udders was on the average about half as high as that of the milk obtained from the same udders before death, and all measures introduced for control of conditions failed to make much difference to this percentage. Injection of petroleum spirit into the udder secretory system, and subsequent withdrawal only increased the butter-fat by about 10 per cent., and not more than 44 per cent. of the injected solvent could be recovered. The percentages of solids-not-fat and of protein and, in the case of the combined group, of lactose, were nearly the same in the first *post-mortem* as in the *ante-mortem* milk, but were distinctly lower in the second *post-mortem* milk. The percentage of ash increased from the *ante-mortem* milk through the first to the second *post-mortem* milk, and the fat-protein ratio followed a trend similar to that of the butter-fat. D. G. H.

Cyanic and Thiocyanic Acid in the Living Organism. J. A. Klaassen. (*Pharm. Weekblad*, 1932, **69**, 1311–1314.)—This is a theoretical discussion of the rôle of sulphur in metabolism. Compounds containing labile sulphur (*e.g.* glutathione) can act as donators for the reaction $CN' \rightarrow CNS'$. This reaction, which destroys the poisonous effects of cyanides, occurs in connection with a number of diseases, and particularly with those of the liver (*e.g.* degeneration of the liver), since this organ contains 0·9 per cent. of sulphur; it is also stimulated in the presence of high concentrations of blood. The results of Schechter (*Z. klin. Med.*, 1931, **117**, 5), which were obtained from 1 grm. of mashed liver and 10 mgrms. of sodium cyanide in the presence of 0·5 c.c. of a 5 per cent. solution of sodium hydroxide at 37° C., are criticised on the ground that the experimental conditions corresponded with abnormal concentrations of cyanide and alkali. Schechter found 2 to 7·5 mgrms. of thiocyanate ion per litre of blood serum, compared with the maximum figure of 0·5 mgrm. given by Kohn–Abrest. The method has also been suggested as a means of evaluating thyroid preparations (cf. *Chem. Weekblad*, 1932, **69**, 655). J. G.

Reducing Value of Plant Juices containing Vitamin *C*, as determined by 2 : 6-Dichlorophenol Indophenol. H. H. Mottern, E. M. Nelson, and R. Walker. (*J. Assoc. Off. Agr. Chem.*, 1932, **15**, 614–616.)—Recent progress towards the establishment of the chemical nature of vitamin *C* has led to attempts to correlate the chemical properties of various substances, particularly their reducing value, with the presence of this vitamin. Efforts to find an inter-relation between the reducing value and oxidative changes in orange juice are now described. When iodine titration is used to fix the reducing value, it is found that the juice retains slight reducing power after the reaction with atmospheric oxygen is apparently complete. Iodine has, therefore, been discarded in favour of 2:6-dichlorophenol indophenol, which is reduced by orange juice. Examination of a few fruit and vegetable juices rich in vitamin *C* reveals a definite correlation between the reducing value and the vitamin *C*-content determined biologically. Raw cabbage juice, which is a good source of vitamin *C*, undergoes rapid diminution in its reduction titration value owing to the presence of hexoxydase (*cf.* Szent-Györgyi, *J. Biol. Chem.*, 1931, **90**, 385), exposure to air for five minutes being sufficient to destroy more than one-half of the titration value. If cabbage is steamed to destroy the enzyme before the juice is pressed out, the titration value obtained is more consistent with biological response. The extent to which titration with 2:6-dichlorophenol indophenol can be relied on to determine the distribution of vitamin *C* requires further investigation, but it is believed that the titration may be useful in detecting destruction of this vitamin in the various stages of the commercial processing of fruits and vegetables. T. H. P.

Bacteriological

Bacteria on Fruit. J. T. Smeall. (*Brit. Med. J.*, 1932, 917–919.)—The micro-organisms present on the surfaces of fruits of various kinds have been investigated qualitatively. Two kinds (Tunis and Iraq) of dates in boxes or

packets were examined, a number of the fruit from the bottom layer in the box being transferred to flasks of broth and incubated. In 16 tests on Tunis dates, which were French-packed, *B. subtilis* and allied organisms, and *Streptococci* were found in all cases, yeasts in 8, *B. coli* in 7 and *Staphylococci* in 7. The *Streptococci* comprised *S. faecalis* (12), *S. mitis* (9), *S. equinus* (2), and *S. Salivarius* (2); *S. faecalis* resisted 60° C. for 30 minutes, and *S. mitis* sometimes proved resistant under these conditions. Nine samples of Iraq dates (packed either in England or in the country of origin) showed *B. subtilis* in 9, and *Streptococci* (*S. faecalis*, *S. mitis*, and *S. salivarius*) in 4 cases. Twenty samples of colonial, continental, and Argentine grapes yielded *B. subtilis* and its allies in all cases, *Streptococci* in 19 [*S. mitis* (15), *S. equinus* (13), *S. salivarius* (3), and *S. faecalis* (2)], *Staphylococci* in 6 cases, and moulds in 1 case. Ten samples of English and French cherries gave *B. subtilis* and allied forms in every instance, *Streptococci* in 9 [*S. mitis* (5), *S. equinus* (5), and *S. faecalis* (4)], and *Staphylococci* in 6 cases, as well as diphtheroids and moulds in 1 case each. In addition, a storm-clot appeared in milk tubes in 11 out of the 55 cases, but the presence of *B. welchii* was not definitely proved.

The wide diffusion of micro-organisms, and the unavoidable handling of fruit between grower and consumer, necessarily results in gross contamination. The vast majority of germs attached to the surface of fruit are harmless, but pathogenic organisms may obviously be deposited at times. Apart both from any definite disease and from the diarrhoea and colic sometimes caused by the ingestion of unripe fruit, it seems likely that some of the minor gastro-intestinal disturbances common during the fruit-eating season may be due to the bacterial content of the fruit. Of the various *Streptococci*, which are generally regarded as saprophytes, *S. faecalis* is present commonly in human, but only rarely in animal, faeces. *S. mitis* may occur in the mouth or intestines of human beings, and *S. salivarius* is a mouth organism, while *S. equinus* is considered to be derived from horse-dung.

The available evidence indicates that the germs present on the surface of fruit do not penetrate the unbroken skin to the edible pulp, but it is found that the typhoid bacillus, emulsified in normal saline and placed on the surface of dates, remains alive after 68 days' storage in the dark at the ordinary temperature. Pathogenic bacteria, protozoan cysts and helminth eggs may be killed by immersion of the fruit in boiling water for ten seconds, but such a drastic measure is scarcely necessary in this country to render fruit reasonably safe. If the skin of fruit is to be eaten, it is recommended that the fruit be washed either in running water or in several changes of water. T. H. P.

Organic Analysis

Determination of Halogens in Organic Compounds by the Sodamide Method. F. Govaert. (*Compt. rend.*, **1932**, **195**, 797–798.)—In the following method [*cf.* Chablay, *Ann. Chim.*, 1914, **1** (ix), 469; Dains, Vaughan and Janney, *J. Amer. Chem. Soc.*, 1918, **40**, 939; Vaughan and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 274], the sodamide method has been modified to render it

applicable to the analysis of substances insoluble in liquid ammonia: To 0·1 to 0·5 grm. of the halogen compound, 30 to 50 c.c. of liquid ammonia are added. If the substance is insoluble in this liquid, 10 c.c. of a solvent for the compound, which need not necessarily be miscible with liquid ammonia, but should be inert to sodamide, are added. The mixture is agitated mechanically to produce an emulsion, and a small piece of sodium (about 0·1 grm.) is added. Ordinarily a blue coloration is produced, and is discharged almost immediately. Further additions of sodium are made until a point is reached at which the bleaching of the blue colour occupies about 2 minutes. The ammonia is then allowed to evaporate, the residue is dissolved in water, and the halogen is determined in the usual manner. The results of analyses by this method of tetrabromopentaerythritol (for which toluene was used as the inert solvent) agreed well with the theoretical values. S. G. C.

Oil of Bittersweet Seed. C. Barkenbus and C. F. Krewson. (*J. Amer. Chem. Soc.*, 1932, **54**, 3993–3997.)—The fruit of the bittersweet vine (*Celastrus scandens*) contains 4 to 6 seeds embedded in the scarlet pulp. The seeds collected over a period of four years yielded 36 per cent. of oil to petroleum spirit, 46·7 to ether, and 53·2 per cent. to ethyl alcohol. The extracted meal contained: Moisture, 3·05; ash, 2·88; protein, 18·94; crude fibre, 9·14; free invert sugar, 0·49; sugar by inversion, 1·60; pentosans, 5·87; and starch, 0·68 per cent. The clear yellow oil had the following characteristics:—Sp.gr. at 20° C., 0·9772; $n_D^{20°}$, 1·4815; saponification value, 297·0; iodine value (Hanus), 121·5; thiocyanogen value, 69·96; Reichert–Meissl value, 70·8; acid value, 3·9; acetyl value, 147·5; unsaponifiable matter, 2·9; soluble acids per cent. as butyric, 18·9; insoluble acids, 70·9 per cent. (with hexabromide value 17·6), unsaturated acids, corrected, 57·1; insoluble saturated acids, corrected, 9·8 per cent. The very high Reichert–Meissl value is remarkable. The percentage composition of the oil was calculated to be: Linolic acid, 38·4; linolenic acid, 21·0; palmitic acid, 8·42; stearic acid, 1·88; soluble acids calculated as acetic (although about equal amounts of formic and acetic acids and a small amount of caproic acid form part of the soluble acids), 15·67; and unsaponifiable matter, 2·96 per cent. D. G. H.

Analysis of Oleines and Stearines. V. Boulez. (*Bull. Mat. Grasses*, 1932, **17**, 298–300.)—*Determination of hydroxy acids in oleines and stearines.*—The saponification and acid values are determined, and subsequently the total saponification after acetylation and the proportion of hydroxy acids then calculated. About 5 grms. of the oleine or stearine are weighed into a flask, followed by about 3 times this weight of xylene (weighed accurately). To the mixture, 15 grms. of acetic anhydride and 1·5 to 2 grms. of melted sodium acetate are added, and the mixture is heated beneath a reflux condenser for 2 hours. When nearly cool, 40 to 50 grms. of water are run in, and after being heated on a water-bath for half an hour, the acid water is run off and the xylene and acetylated acids are washed with water, and dried over anhydrous sodium sulphate. A few grms. of the dry mixture are weighed, warmed with alcohol, and titrated with alkali. An excess of alkali is then run in, the mixture saponified, and the excess of alkali found.

Determination of the acetyl value in castor oil.—Five to 10 grms. of oil, 25 c.c. (weighed) of xylene, 20 to 30 grms. of acetic anhydride, and 0·5 to 2 grms. of fused sodium acetate are heated beneath a reflux condenser for 2 hours, and when nearly cool, 50 grms. of hot water are added, and the mixture is warmed for half-an-hour to destroy the acetic anhydride, poured into a separating funnel, and treated as above. To a weighed, filtered portion of the dry xylene mixture, 25 c.c. of 0·5 *N* sodium or potassium hydroxide solution are added, the mixture is heated to effect saponification, excess of 0·5 *N* hydrochloric acid is added, and the excess is determined by titrating with alkali. Values found for medicinal and industrial castor oils, respectively, were: Saponification value before acetylation, 187, 185; total saponification value, 356 and 361; acetyl value, 169 (corresponding with ricinoleic acid, 89·98 per cent.) and 176. D. G. H.

Determination of Buffer Salts and Acidity in the Aqueous Extracts of Vegetable-tanned Leathers. C. W. Davies and R. F. Innes. (*J. Inter. Soc. Leather Trades Chem.*, 1932, **16**, 546.)—The quantity of buffer salt and the nature of free and combined acids present in a leather can be determined by the shape of the conductivity-titration curves of the aqueous extract. Typical curves of the following acids are given and discussed:—Hydrochloric, sulphuric, acetic, lactic, and a mixture of hydrochloric and acetic; also of the aqueous extracts of leathers tanned with single tanning materials—Nigerian acacia pods, sumac (rich in buffer), gambier (some buffer), oak-bark, chestnut, mimosa and quebracho (no buffer). Curves are also given for a new bookbinding leather containing sulphuric acid, for the protected and exposed portions of an old bookbinding which had rotted, and finally for sumac-tanned and mimosa-tanned leathers to which 1 per cent. of sulphuric acid had been added. It is shown that the high acidity of chestnut-tanned leather is not due to acetic acid, as is generally assumed.

It is suggested that the method may be used to decide whether a leather has been treated with mineral acid in insufficient quantity to decompose all the buffer salts present. R. F. I.

Detection and Determination of Zinc and Magnesium in Sized Cotton. A. Geake. (*J. Text. Inst.*, 1932, **23**, 279T.)—The quantitative tests described are the oxine method for zinc and magnesium and an electrometric method for zinc. For the latter the sized warp is extracted with hot dilute acid. It is necessary, however, to evaporate the extract to dryness and remove the organic matter by "acid ashing" with nitric and sulphuric acid before electrolysis. The oxine method, though no more accurate, is more convenient; it depends on the fact that oxine (8-hydroxyquinoline) precipitates zinc alone in slightly acid solution. Zinc and magnesium may be precipitated together from the filtrate by rendering it alkaline. About 10 grms. of the yarn or cloth are digested for half an hour on a boiling water-bath with 130 c.c. of water and 20 c.c. of *N* hydrochloric acid. The solution is filtered, and the filtrate and washings are diluted to 250 c.c. For the determination of the zinc, 50 c.c. of the solution are treated successively in a 100-c.c. conical flask with 4 c.c. of 2 *N* acetic acid, 2·5 c.c. of *N* ammonium acetate solution, an excess of fresh 5 per cent. alcoholic oxine solution, and 4 c.c. of *N*

sodium hydroxide solution. The mixture is heated to boiling, kept hot for half an hour, and filtered, and the precipitate is washed 3 times with hot water, and then dissolved in 100 c.c. of hot 2 *N* hydrochloric acid. After cooling, 1 c.c. of a 0·005 per cent. solution of methyl red is added, and the solution is treated with a solution containing 2·784 grms. of potassium bromate and 12 grms. of potassium bromide per litre until the methyl red indicator is pure yellow, and the bromate and bromide solution are in sufficient excess to bleach the indicator. After one minute this excess is determined iodimetrically (one c.c. of 5 per cent. oxine solution is equivalent to 13·8 c.c. of the 0·1 *N* bromate-bromide solution). If the zinc chloride is present to the extent of 0·5 per cent. it will require 1·7 c.c. of the 5 per cent. oxine solution.

For the determination of magnesium 25 to 50 c.c. of the 250 c.c. of solution are heated to boiling, 1 c.c. of saturated ammonium oxalate is added, and the solution is made just alkaline to methyl red by adding 5 *N* ammonia. After the calcium is precipitated, 2 c.c. of 5 *N* ammonia, an excess of fresh 5 per cent. alcoholic oxine and a further 2 c.c. of 5 *N* ammonia are added. The volume of the oxine solution should be about 1 c.c. in excess of that required to precipitate both zinc and magnesium. The mixture is heated on a water-bath for 1 hour, the precipitate is filtered off, washed and dissolved in acid and the two metals are determined (in terms of zinc) as described for zinc oxinate. The percentage of magnesium chloride in raw cotton varies from 0·21 in Texas to 0·30 in Egyptian.

When freshly manufactured, cloth contains the zinc chloride entirely on the sized warp. If stored at 87 per cent. relative humidity for only 5 days zinc will be found also on the weft, whereas if stored dry for a long period there is no diffusion of the zinc chloride.

Aluminium may be detected in cotton goods by adding, to 1 c.c. of a 0·2 *N* acetic acid extract, 1 c.c. of a 0·1 per cent. solution of Eriochromcyanine R, followed by 2 *N* sodium hydroxide until alkaline and 0·2 *N* acetic acid until slightly acid. The presence of aluminium causes the development of a deep blue tint with formation of a precipitate. The colour-change between 0·001 mgrm. and 0·005 mgrm. of aluminium is very sharp. This test may be utilised for the detection of china clay in cloth, the presence of silica being confirmed by means of its reaction with molybdic acid.

Fluorine may be detected qualitatively by mixing the ash of the cloth with powdered silica, heating with strong sulphuric, which is added slowly, and passing the evolved gases through water, when, if fluorine is present, the hydrofluosilicic acid is decomposed, with formation of a gelatinous precipitate of silica.

R. F. I.

Inorganic Analysis

Observations on the p_H values of Hypochlorite Solutions. L. P. Lynch and C. R. Nodder. (*J. Text. Inst.*, 1932, **23**, 309T.)—The excess of alkali usually present in hypochlorite solutions may be determined by titration with methyl red as indicator, provided the hypochlorite has been made to decompose; treatment with neutral hydrogen peroxide is satisfactory for this purpose. The p_H value

of a solution of hypochlorite after such treatment is lower than before (if buffer salt is absent), because of the formation of hydrochloric acid, which may decrease the p_H value to 5·0. Hypochlorous acid having a dissociation constant $1·0 \times 10^{-8}$, a solution of pure sodium hypochlorite of a concentration of $N/25$ in available chlorine will have the p_H value 10·1.

The most reliable simple test for the determination of the p_H value of "chemics" is carried out as follows:—A Whatman No. 5 filter paper, 9 cm. in diameter, is folded four times, and a drop of the solution to be tested is placed on the 8-fold edge and allowed to soak in. Four or five further drops are added singly, and as soon as the last is absorbed 0·05 c.c. of B.D.H. "universal indicator" is dropped on to the wet area of the paper. The colour produced is compared with that obtained with buffered solutions of the same available chlorine-content and of known p_H value prepared with sodium barbitone solutions. A bluish spot with a violet rim indicates a p_H value exceeding 10·0. Barbitone has an ionisation constant very similar to that of hypochlorous acid. Equations are given from which the change in p_H value produced by adding the sodium salt of weak acid to a buffer solution may be determined, and also the ionisation constant of the weak acid.

R. F. I.

Determination of Zinc in Aluminium and Aluminium Alloys. H. Wagner and H. Kolb. (*Chem.-Ztg.*, 1932, **56**, 890–891.)—In tests of a commonly-used method for the determination of zinc in aluminium and its alloys, in which the zinc is deposited electrolytically from the solution obtained by disintegrating the metal with sodium hydroxide solution, values in excess of the true zinc content were obtained. The errors were traced to a small proportion of the iron-content of the metal having passed into solution together with the zinc and been deposited with it on the cathode. It is recommended that the deposit of impure zinc be dissolved and the weight of the co-deposited iron determined and deducted.

S. G. C.

New Method for the Separation of Zinc, Cobalt, Nickel and Iron from Aluminium, Chromium and Manganese. E. H. Swift, R. C. Barton, and H. S. Backus. (*J. Amer. Chem. Soc.*, 1932, **54**, 4161–4172.)—This paper is Part III of a series of reports of studies of various methods for the separation of the common elements into groups, Parts I and II (*id.*, 1932, **54**, 2219, 4155) having dealt respectively with (i) the ammonia precipitation method, and (ii) the sodium hydroxide and sodium peroxide method. It has been found that zinc, nickel, cobalt and iron can be separated from aluminium, chromium and manganese by precipitation with hydrogen sulphide from a solution (about 100 to 200 c.c.) containing a limited excess of sodium bicarbonate (about 1 grm.) and sufficient oxalate to prevent the precipitation of aluminium and chromium. The method adopted for the precipitation is as follows: A rapid stream of hydrogen sulphide was passed through the solution for 3 to 5 minutes, and then, while a slow flow of the gas was maintained, the liquid was heated to 60 to 80° C. The solution was then tested with litmus, and, if acid, it was neutralised with a further quantity of sodium bicarbonate, and 1 grm. of the solid was added in excess; the passage of hydrogen

sulphide was continued for 3 to 5 minutes. This process was repeated until the solution remained slightly alkaline to litmus; in no case were more than three 1-grm. portions of sodium bicarbonate required. The liquid was filtered at once, and the precipitate was washed with a hot solution prepared by dissolving 1 grm. of ammonium oxalate in 100 c.c. of hot water and saturating it with hydrogen sulphide; the addition of 0·5 grm. of sodium bicarbonate to this solution before saturating it with hydrogen sulphide was found advantageous in washing ferrous sulphide. The sulphide precipitates are stated to be obtained in a form which is readily filtered off and washed. The method is proposed for the qualitative separation of these metals into groups. Experiments showed that 1 mgrm. of any element of one group can be separated from 500 mgrms. of any element of the other group. As a quantitative method it is shown that 250 mgrms. of any element of the "zinc group" can be precipitated quantitatively from a solution containing 250 mgrms. of any element of the "aluminium group," and less than 1 mgrm. of the latter is carried down in the precipitate. S. G. C.

Colorimetric Determination of Ferric Iron with 7-Iodo-8-Hydroxyquinoline-5-Sulphonic Acid. J. H. Yoe. (*J. Amer. Chem. Soc.*, 1932, **54**, 4139–4143.)—7-Iodo-8-hydroxyquinoline-5-sulphonic acid dissolves in water to yield a bright yellow solution, which, when mixed with a very dilute solution of ferric iron rendered faintly acid to methyl orange paper, produces a greenish-yellow to dark green colour, the shade and intensity of which vary with the concentration of iron. The reaction may be applied quantitatively by comparing the colours produced on adding a similar quantity of a 0·2 per cent. aqueous solution of the reagent to the test solution and to a range of standard solutions of iron contained in Nessler tubes. The reaction is sensitive to 1 part of iron in 10 million parts of solution. The colour is stable to light, but is destroyed by an excess of acid or alkali. Tests with solutions containing the common elements, platinum metals, rare earths, etc., showed that these give no characteristic colour-reaction with the reagent; none of the colourless ions interfere with the reaction for iron, and coloured ions interfere only when in sufficient concentration to prevent accurate colour matching; cupric ions are exceptional in giving with the reagent a white, finely divided precipitate when present in amount greater than a few parts in 10 million parts of solution. No colour-reaction with the reagent is given by ferrous iron. S. G. C.

Determination of Silicon and Aluminium in Presence of Fluoride and Orthophosphate. T. Millner and F. Kunos. (*Z. anal. Chem.*, 1932, **90**, 161–170.)—(1) *Silicon in alkali fluorosilicate.*—A weighed amount of, *e.g.* potassium fluorosilicate (0·4 to 0·04 grm.) is added to a solution of boric acid (1·2 to 0·5 grm.) in a platinum basin. After treatment with about 1 c.c. of strong sulphuric and 4 to 5 c.c. of strong hydrochloric acid, the solution is evaporated on a water-bath, and then over a free flame until white fumes are given off. When cold, 25 c.c. of water are added, and then sodium hydroxide to alkaline reaction. The liquid is treated with 5 c.c. of strong hydrochloric acid, and the silica determination is concluded in

the usual manner. (ii) *Silicon in presence of fluoride and orthophosphate.*—The solution of fluorosilicate (0·025 to 0·0005 grm.) in a platinum dish is treated with 0·5 grm. of boric acid and 0·2 to 0·1 grm. of sodium phosphate. The liquid is evaporated to dryness with 3 to 5 c.c. of strong hydrochloric acid; this treatment is repeated twice more, and the silica is dehydrated by 2 hours' heating at 130° C. The determination is completed as usual. (iii) *Aluminium in presence of fluoride and orthophosphate.*—The weighed portion of cryolite in a platinum basin is treated with about 0·5 grm. of boric acid and a solution of phosphoric acid (10 times as much P_2O_5 as the Al_2O_3 to be determined), and evaporated three times with a few c.c. of strong nitric acid. The residue is dissolved in hot dilute nitric acid and the solution is treated with ammonium molybdate (Woy's directions). The filtrate from the yellow precipitate is evaporated to dryness, and the residue is gently ignited for the removal of ammonium salts; the residue is warmed with 20 c.c. of 2 *N* sulphuric acid, and 20 to 30 c.c. of water, and ammonia (1 : 1) is added until faintly alkaline. The insoluble matter goes into solution and aluminium hydroxide is precipitated. The liquid, transferred to a beaker, is kept on a water-bath for 3 to 4 hours; after standing overnight, the precipitated alumina is collected and determined as usual. (iv) *Silicon and aluminium in presence of fluoride and orthophosphate.*—The manipulations are substantially the same as under (ii). For 0·1 grm. of silica and 0·15 grm. of cryolite, the additions are 1 grm. of boric acid and enough sodium phosphate to provide 10 parts of P_2O_5 to one of Al_2O_3. The silica is obtained by three evaporations with hydrochloric acid, drying at 130° C., digestion with strong hydrochloric acid on a water-bath for 15 minutes, dilution, and filtration. The filtrate is evaporated to dryness, the chlorides converted into nitrates, and the phosphoric acid removed and alumina precipitated as under (iii). (v) *The determination of fluorine and orthophosphate* in presence of silica and alumina is being investigated. W. R. S.

Volumetric Determination of Rhenium. J. G. F. Druce. (*Chem. News*, **1932, 145**, 186–187.)—The neutral solution of potassium perrhenate is titrated with 0·02 to 0·05 *N* silver nitrate solution, potassium chromate being used as the indicator. The calculated value for Re was in fairly good agreement with Hönigschmidt and Sachtleben's figure 186·31. Phosphate, arsenate, tungstate, and molybdate interfere. W. R. S.

Microchemical

Micro-Combustion of Carbon and Hydrogen. P. L. Kirk and A. G. McCalla. (*Mikrochem.*, 1932, **12**, 87–97.)—Ter Meulen and Heslinga's method (*Neue Methoden der organisch-chemische Analyse*, Leipzig, 1927) has been adapted to the micro-combustion of samples of the order of 2 mgrms. by combining this method with the Pregl technique for the control of gas-speed and pressure and the weighing of absorption tubes. The combustion is carried out in pure oxygen, which must be pre-heated if it contains any organic impurity. Pregl's pressure-regulator and bubble-counter are used, but askarite and anhydrone replace soda-lime and calcium chloride for the absorption of carbon dioxide and water,

respectively. The combustion-tube is packed, as in the Ter Meulen method, with ignited asbestos, a layer of lead peroxide, then a short layer of catalytic manganic oxide, followed by an asbestos plug at the junction between the small constant-temperature bath and the long heater. A long layer of catalytic manganic oxide, to be heated by the long heater, completes the filling. The catalytic tube filling appears to last indefinitely; it is prepared by the method described by Rogers, Piggot, Bahlke and Jennings (*J. Amer. Chem. Soc.*, 1921, **43**, 1973). The portion of the tube containing the catalyst is heated to 400° C. by means of a simple electric heater; that containing the lead peroxide is heated by a Pregl constant-temperature bath in which phenol is boiled. The long condenser-chimney must be closed with a calcium chloride tube to prevent ingress of water. The combustion tube is joined by an outside rubber connection to a tube of the same bore, drawn out at one end, instead of by a rubber stopper with a tube through the middle. The combustion is carried out with a movable Bunsen burner as in the Pregl method. The absorption-tubes are weighed full of oxygen. Excellent results were obtained with a large number of compounds containing carbon, hydrogen, oxygen, nitrogen, sulphur, and halogens. J. W. B.

A Simple Micro-Soxhlet Extractor. A. Wasitzky. (*Mikrochem.*, 1932, **11**, 1–6.)—A micro-Soxhlet apparatus, designed for the extraction of lipoids from biological material, is made from a thick-walled test-tube, approximately 20 cm. long and 2·5 cm. wide, constricted to a waist about 7 cm. from the bottom. The bore of the constriction is approximately 1·2 cm. The extraction vessel rests on the constriction and is made from a test-tube, 5 cm. long and 1·2 cm. in diameter. A narrow siphon-tube leads from the bottom, is bent round and up nearly to the top of the vessel and then bent back to lead through the constriction in the outer tube. The condenser consists of a small test-tube through which water circulates from two tubes fitted into the neck with a rubber stopper, or joined into the condenser. For extractions under ordinary pressure the condenser rests on the neck of the apparatus. For extractions under reduced pressure the condenser is fitted with a ground-glass joint, and the apparatus has a side tube for connection with the pump. Determinations of cholesterol and lipoid phosphorus in dry milk powder on 1-grm. samples in the micro-extractor and on 25-grm. samples in a macro-extractor agreed well. J. W. B.

Sensitive Reaction for Caffeine applicable to Vegetable Tissues. A. Martini. (*Mikrochem.*, 1932, **12**, 109–111.)—On evaporating a drop of gold chloride solution (10:100) with a drop of caffeine hydrochloride solution (1:1000), bright yellow prisms are formed. The sensitiveness of this reaction is increased when a drop of a saturated solution of sodium bromide is added. The solution becomes red, and star-like groups of needle-shaped orange-yellow crystals are formed. The reaction is perceptible in dilutions of 1:2000 of caffeine hydrochloride. The compound formed is probably an aurobromide of caffeine, $C_8H_{11}N_4O_2$, $AuBr_4$, $2H_2O$. The reaction, which does not take place with theobromine under the same conditions, is visible when microscopic sections of plant material containing caffeine are used. J. W. B.

New Micro-chemical Reaction for Cocaine. A. Martini. (*Mikrochem.*, 1932, **12**, 111–112.)—The reagent is a slightly yellow solution of potassium lead iodide ($KPbI_3$), prepared by precipitating yellow lead diodide (PbI_2) from 1 per cent. lead nitrate solution with a saturated solution of potassium iodide, and dissolving the precipitate in excess of potassium iodide solution. When a drop of a 1:1000 solution of cocaine hydrochloride is treated with a drop of the reagent a white precipitate is formed which shows a typical crystalline appearance under the microscope; the reaction is clearer when the cocaine solution is treated with a drop of acetone before the addition of the reagent. Morphine, codeine, strychnine, atropine, apomorphine, sparteine, quinine, nicotine, narceine, etc., either give no reaction or form only an amorphous precipitate. When bromide is substituted for iodide in the reagent similar crystals are formed, but the reaction is less sensitive. J. W. B.

Reviews

WILEY'S "PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS." Volume II. FERTILISERS AND INSECTICIDES. Third Edition. Edited by C. A. BROWNE and W. W. SKINNER. Pp. xvi+646, with 65 illustrations. Chemical Publishing Co., Inc., Easton, Pa., U.S.A.

The edition under review is the third, and it has been prepared and issued under the direction of the American Association of Official Agricultural Chemists. The original volume was written by the late Dr. H. W. Wiley with a view to enabling teachers, students and analysts to appreciate the principles underlying the science and art of analysis. As age and failing sight rendered intimate contact with the progress of agricultural chemistry difficult, Wiley presented the copyright of his works to the Association of Official Agricultural Chemists; the new volume is the outcome of the joint labours of several contributors. The work is intended to supplement the well-known *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists.*

The first pleasing feature to be well noted in the new edition is that it contains fewer pages than its predecessor; yet the authors have been able to embody all the information considered of value in the second edition, and to add much new matter. Would that all authors of new editions might treat their readers with such consideration.

The book is very properly divided into two parts: the first, consisting of 474 pages, deals with fertilisers, and the second part (140 pages) with insecticides and fungicides.

In America the term "manure" is applied only to animal excrements with or without litter, and the term "fertiliser" is reserved for any other materials which may furnish plants with one or more of the elements necessary for normal growth, but apparently some potash salts have been named "Potash Manures." The title of the book, then, indicates that information is restricted to fertilising materials other than those typified by farmyard manure.

An early chapter deals with the varying methods of expressing the results obtained on analysis and reminds all concerned that reports are frequently required by people who are not chemists; though a new system of reporting may contain terms implicating greater scientific accuracy, it should be capable of being easily understood by those requiring a report. In this country we are aware that the farming community still thinks of nitrogen in terms of ammonia and of phosphorus in terms of calcium phosphate, and these instances emphasise the importance of making gradual any change in a system of reporting.

A short chapter on sampling provides much information and contains many illustrations of grinding apparatus. But perhaps the chapter does not stress sufficiently the importance of giving that attention to sampling which would invariably result in the small sample submitted to the laboratory being representative of the bulk. How many analytical differences obtained in laboratories have been due to careless sampling! This chapter also suggests that a sample which is reasonably dry and not caustic or acid may be placed in paraffined paper bags to facilitate transport to the laboratory. This procedure might well be adopted when loss of moisture is not to be feared, enabling samplers to have recourse to receptacles other than glass jars, which so frequently arrive at their destination in a broken condition. The 24 pages devoted to the occurrence and determination of moisture in fertilisers are of importance, for they contain the official methods used in many countries.

Information concerning the determination of phosphoric acid and the sources of phosphates very rightly occupies a considerable portion of the book. It is somewhat strange that under the description of bone products no mention is made of the nitrogen they contain, and, further, that the table showing the composition of typical samples does not state that any nitrogen is contained in raw bone or bone-meal, etc. In fact, the compositions of raw bone and bone-meal would appear to be identical, and this applies also to bone-charcoal and bone-ash.

Special consideration is given to nitrogen, its occurrence, its sources, and its agricultural uses. The chapter on the utilisation of the nitrogen of the air by the manufacture of salts containing nitrogen is interesting, and probably few realise that in 1929 the world's nitrogen-fixation capacity amounted to over 1,800,000 tons. Many chemical methods are quoted for the determination of nitrogen in its several forms as used by agriculturists. The Street permanganate method for testing the quality of insoluble organic nitrogen is reviewed, and the further work carried out on this important subject is more or less briefly described. The Street process, however, has not been very favourably received in this country, but for some purposes this process, or a carefully standardised modification, might be extremely useful.

Valuable information with regard to the occurrence, and the methods in use for the determination, of potassium is placed at the disposal of the reader.

The last portion of the work deals with insecticides and fungicides. In America the Federal Insecticide Act has a very wide application, and entails the examination of insecticides and fungicides. Therefore, the Act has directed attention to the sampling and analysis of insecticides. The subject may assume greater importance in this country, for a Bill to control the purity, etc., of

insecticides may at any time be promoted. For the sake of convenience the authors have grouped insecticides into chemical classes and have dealt with these under headings such as Arsenicals, Copper Compounds, Sulphur Compounds, Coal Tar Products, etc. Methods are described for the determination of arsenic, lead, copper, etc., and the process applicable in particular circumstances is given. The methods of analysis for lime sulphur are inadequate, but this may be due to legal requirements rendering the examination of lime sulphur unnecessary. English chemists should, at all events, bear in mind the excellent work carried out in this country by Goodwin.

The work is an excellent survey of knowledge covering the occurrence and sources of fertilisers and of the methods for determining various constituents of value to plants. With the continued growth of the commercial use of insecticides and fungicides, the information afforded will become of increasing importance to chemists, teachers and others.

F. W. F. ARNAUD

BIBBY'S BOOK ON MILK. Section I, Supplement No. 2, etc. Pp. 46+18. Liverpool: J. Bibby & Sons, Ltd. 1932. Price 4s. net.

The writer of this collection of pamphlets (obviously written or inspired by Mr. John Hanley) pays a subtle but possibly unconscious compliment to Public Analysts when he naively says (page 7): "The suspicion has recently dawned upon the writer that possibly his mental attitude is essentially different from that of many of his professional brethren on the probabilities of the position." That this has only happened recently is certainly no fault of Public Analysts, who for years have been trying to impress Mr. Hanley with the fact that his is a voice crying—not in the wilderness—but in the crowded township of unanimous disagreement. We are getting on; perhaps, in years to come, Mr. Hanley may at last realise that a man with opinions diametrically opposed to those of the whole of his co-workers is not necessarily right.

The matter submitted for review consists of one longer pamphlet and three small leaflets. The leaflets are reprints from various local newspapers, and give accounts of three recent cases in which Mr. Hanley claims to have been successful in getting the defendant discharged from the prosecution. There is no mention, however, of the two recent appeal cases in the North-West—in each of which the defendant, supported by Mr. Hanley, had his appeal dismissed with costs—nor of the case in South Staffordshire in which the Stipendiary Magistrate remarked that the defendant's heavy costs were largely due to the enthusiasm of Mr. Hanley. Other cases of a similar nature appear to have been overlooked, but not so a few lines reprinted from the *Bootle Times* of September 16th, 1932. As these occur in two separate places they seem to be of sufficient importance to quote: "Mr. John Hanley, of Bootle, who was successful in refuting the freezing-point test in a milk prosecution at Bootle, has been able to do likewise in a number of similar cases in various parts of the country. One of the most recent was at Taunton, where, he said, he did not agree that the freezing test could be relied upon, because he had found it to vary considerably." Those who read that Mr. Hanley has been

using the Hortvet method for the past 25 years (p. 5 of the Howden-le-Wear leaflet), who know that Hortvet's original paper was published as late as 1921, and who remember that Mr. Hanley told the World's Dairy Congress at Reading in 1928 that he could make nothing of the test, but was persevering with it, may not wonder that he has found it to vary considerably. They may, however, wonder why the evidence of a worker who, on his own showing, could not make anything of a test in twenty years, should be taken seriously after a further five.

In supplement No. 10, in a case in which the test for nitrates had not been carried out by the Public Analyst, Mr. Hanley stated, "I think it is most important; it is the only positive test usually available to a public analyst," whilst in Supplement No. 13, where the test for nitrates was being relied upon by the Public Analyst, Mr. Hanley declared that there was no positive test to detect added water in milk. He explains this in the *Farmer and Stockbreeder* of October 31st, 1932, by saying that "one has to consider the circumstances in each case," and goes on in an attempt to explain them, but there is no mention of any such explanation in the accounts of the cases themselves.

The larger pamphlet of forty-six pages consists of two main portions. The first deals *inter alia* with the variations in the milk of one cow and of a herd of five cows from day to day, the second with the question of what constitutes normal milk; it is maintained that normal milk is the milk of healthy, reasonably well-kept cows. There would appear to be no objection to this definition, provided that it be not assumed that such normal milk necessarily has a normal composition. It is well known that Mr. Hanley objects to the term "abnormal" for a milk which is naturally very poor, but to the reviewers a genuine milk containing, say, 1·7 per cent. of fat and 7·1 per cent. of solids-not-fat is very definitely abnormal, that is, out of the ordinary, and they would be convinced to the contrary with the greatest difficulty.

To the general analytical results very little objection will be taken, but the methods of presenting them are unnecessarily complicated, while the compilation of the tables and graphs must have entailed a tremendous amount of labour, much of which has been wasted. Many Public Analysts will be delighted, even if a little surprised, to know that the variations which Mr. Hanley finds in the milk of a herd of five cows, from day to day for a month, are such as they themselves would have expected, and that they can be used quite profitably in the presentation of their cases in Court. There are, however, many small details and interpolations to which attention must be drawn or serious objection taken.

We read "Aberdeen county is the only authority in Great Britain and Ireland which takes full advantage of the procedure of appeal-to-cows and conducts the process accurately," and later on we find "Public Analysts in general admit they have found the milk of single cows below the presumptive limits, but never a herd." In these connections it would be interesting to know on what evidence such statements have been made.

Mr. Hanley quite cheerfully states that his freezing-points, determined with the Hortvet apparatus, have been corrected by the use of the Raoult corrections, as applied by Monier-Williams, apparently entirely oblivious of the fact that Hortvet especially designed his apparatus to avoid corrections so far as possible,

and that all the American results are given *uncorrected*. This point will doubtless account for the high values given by Mr. Hanley in connection with certain samples of genuine milk. Moreover, in spite of this application of unnecessary corrections, the *highest value* here given for the freezing-point of milk of a hard or of an individual cow is $-0{\cdot}523°$ C.—a figure which, after the corrections wrongly applied have been replaced, agrees well with those of other workers.

On page 5, Mr. Hanley gives the refraction of the milk of an individual cow low in solids-not-fat as 35·62. Those who have followed the controversy between Mr. Hanley and the present reviewers will see that this one figure practically admits the whole principle for which the latter have been contending.

All Public Analysts should read these pamphlets, from which they will learn (unfortunately only in outline) of a method for the detection of added water in milk by microscopic examination of the ash. If this is the positive test for which the author has been looking, and which he says means so much to him, it should be published at the earliest opportunity; should it prove successful, doubtless Public Analysts will be as complimentary to Mr. Hanley as Mr. Hanley has been to them.

G. D. ELSDON
J. R. STUBBS

EXPLOSIVES. Vol. III. By ARTHUR MARSHALL. Pp. 286. London: J. & A. Churchill. 1932. Price £2 2s.

Fifteen years have elapsed since the publication of the first two volumes of this work (*cf.* ANALYST, 1917, **42**, 259, 321). These appeared during the War, and it was consequently not permissible to publish all the developments in explosives which had taken place up to that date. In view of this, and of the large amount of research which has been published since the War, a supplementary volume dealing with the more recent work was greatly needed.

The present volume follows the same sequence of chapters as Volumes I and II, and marginal references to the page-numbers of the original work facilitate reference. Thus the advances in each branch of the subject are readily seen. Numerous references to the literature are given, and a large amount of ground is covered in the space available. The changes which take place in nitric acid at different concentrations and in presence of sulphuric acid are discussed on the basis of Hantzsch's work. Starting from oxonium nitrate in aqueous solution, the acid passes into the pseudo-condition in concentrated form, and in presence of sulphuric acid is largely converted to nitronium sulphate. These transformations have an important bearing on the nitration of cellulose, etc., by mixed acids. The information on the nitro-aromatic compounds, which was rather limited in the original work, has been considerably supplemented. A number of the modern methods of manufacture of compounds used for explosive purposes, including the continuous processes for the manufacture of nitrobenzene, trinitrotoluene, picric acid, and nitroglycerine are described. Newer methods of manufacture of the ingredients of mixed explosives, solvents, etc., are also included. Since the original work a number of new compounds have been introduced as explosives or as ingredients of explosives. The information on manufacturing methods includes some developments in plant construction and the use of acid-resisting materials. It is surprising

however, that so little reference is made to the advances in nitrogen-fixation, which have an important bearing on the manufacture of explosives. A useful feature is the inclusion of numerous tables giving thermo-chemical data, comparative figures for the physical properties of explosives, melting-points, eutectics, etc., as well as valuable statistics showing the relative quantities of different explosives used in this and other countries. Safety precautions are described, and the danger to health resulting from the handling of various nitro-compounds is dealt with in some detail. The methods of testing chemical stability have been considerably amended, as research in this field has been active in recent years. Reference is made to Mayrhofer's modification of the Bergmann and Junk test, the Taliani test, Angeli's acidity test, and the work at Woolwich and by Hansen, Metz, etc., on p_H measurements. The chemical changes which take place in stabilisers during storage are also described.

The sections on analytical methods and physical tests, such as velocity of detonation, sensitiveness, etc., have been amended by the addition of some more recent methods. Finally, an index comprising nearly 4300 entries, and covering the whole three volumes, is included. The volume is readable and is very clearly printed.

R. C. FARMER

VOLUMETRIC ANALYSIS. By G. FOWLES, M.Sc., A.I.C. Pp. xii+202, with 5 figures and 1 coloured plate. London: G. Bell & Sons. 1932. Price 6s.

This volume is intended for the use of students, and, whilst no particular syllabus is followed in its production, sufficient material is included to furnish all that is necessary for many of the higher examinations.

The contents of the book include an introduction; the calibration and use of volumetric apparatus and solutions; the use, theory, and selection of indicators, especially in their application to evaluation of p_H; acidimetric, alkalimetric, oxidation, iodimetric, and precipitation processes; and a concise but detailed synopsis facilitating reference to the various methods described for determining compounds, radicals and elements.

This volume has many excellent features, emphasis being rightly laid throughout the text on the importance of accuracy (for which reason some widely-used methods are omitted), and the section on p_H values and buffer action is the most lucid that the reviewer has yet seen. The text is unusually free from errors of all kinds, and considerable care has been taken to provide clear and exact descriptions of the methods, which include many that are too infrequently employed, although of undoubted value. The general style of the volume is admirable, the index is exhaustive and accurate, and the coloured plate depicting the colour-changes of seven indicators throughout the whole range of p_H values is highly educative. This work will prove a sound and reliable text-book for students, and, as a summary of some of the more recently evolved methods, is worthy of attention from the practising analyst.

T. J. WARD

MODERN METHODS IN QUANTITATIVE CHEMICAL ANALYSIS. By A. D. MITCHELL, D.Sc., F.I.C., and A. M. WARD, Ph.D., D.Sc., A.I.C. Pp. xi+178. London, New York, Toronto: Longmans, Green & Co. 1932. Price 6s.

This interesting and stimulating little book is intended by its authors to be used as a supplement to the standard text-books, primarily in the training of advanced students, by giving a critical selection of analytical methods "introduced or perfected within the last decade." Some processes of more general application are described first (pp. 1–26); they include volumetric iodate and ceric sulphate methods, the use of Jones's reductor, oxidation-reduction and adsorption indicators, and the analytical application of complex compounds. The remainder of the book is devoted to elements (including many "rarer" ones, even rhenium), radicals, and certain organic compounds (amino-acids, cyanamide products, formaldehyde, sugars, urea), described in alphabetical order. Electrometric and micro-methods are not included.

As stated in the preface, the authors were guided by certain theoretical and practical considerations in collecting suitable methods from the contemporary literature. Judicious selection from among the enormous output of recent years is in itself no mean task; but the volume under review represents a much more extensive undertaking, as the authors have actually tested the great majority of the processes described, and the particulars given in the book specify the conditions (which in some cases differ from the original ones) under which they have obtained the best results. Two examples of the authors' critical attitude may be given: (1) "We did not obtain satisfactory separations by the method of Moser and Niessner [beryllium from aluminium], possibly owing to insufficiently definite specification of the acidity conditions in their description" (p. 43). (2) "This method [titration of halides] is described because of its simplicity and ingenuity, although in our hands it has led to slightly high results for iodide, and has occasionally given erratic results for bromide" (p. 87).

Only in a very few instances does one feel tempted to question the advisability of including a particular process in this useful collection. For example, the reviewer wonders what advantages, if any, the phenylthiohydantoic acid process for cobalt may offer over the usual procedures, in which more readily obtainable reagents are applied.

In the general discussion on tannin adsorption complexes (p. 21), a statement to the effect that tannin is a precipitant for earths in presence of tartaric acid would have added to the usefulness of that section. In particular, the simple method by which a small amount of alumina is separated from much iron might have been added.

The book is attractively produced and practically free from misprints. It is sure to appeal strongly to advanced students and research workers, and equally so to the busy professional analyst, as an epitome of progress in analytical chemistry.

W. R. SCHOELLER

IL POLAROGRAFO: SUA TEORIA E APPLICAZIONI. By GIOVANNI SEMERANO. Pp. 207. Padua: A. Draghi. 1932.

Heyrovský's ingenious method of electrolysis, which makes use of the dropping-mercury cathode and is rendered automatic by means of the polarographic arrangement, has now passed out of its probationary period and has become of practical value. The possibility of studying different problems under conditions exactly reproducible, with a minimum expenditure of time and with the added advantage that the diagrams obtained serve as records of the results, is sufficient to account for the ever-increasing uses to which this method of analysis is being applied.

As the subject is of interest, not merely in such varying branches of study as biology, physics, medicine, pharmacy, mineralogy, and geology, but also in the investigation of sugars, explosives, metals, petroleum, dyestuffs, etc., the bibliography is naturally extensive. It is, therefore, a great convenience to have presented, in a single small volume, the theoretical foundations and the practical details of polarographic methods, together with a number of their applications to scientific and industrial problems.

The book is clearly written, and should be understood without difficulty by those who are able to read simple Italian and have some knowledge of physical chemistry. A bibliography, comprising references to over one hundred papers, is appended.

T. H. POPE

B.D.H. REAGENTS FOR "SPOT" TESTS. Pp. 39, 8vo. Published by The British Drug Houses, Ltd. Price 2s. 6d.

This book contains a list of 36 reagents available for the detection or determination of small quantities of metals or other substances. Some of these reagents are quite common substances, such as resorcinol or hexamethylenetetramine. Each reagent is accompanied by a short description of its uses and references to original papers. Unfortunately, the references are few; if a little more trouble had been taken to make them complete, the value of the book would have been greatly increased.

Since the book gathers together a certain amount of information which is scattered throughout the literature, it should prove useful to analysts, so far as it goes, but one cannot help wishing that it went a little further. Of course, one must recognise that it has a limited aim and is published at a low price, but may one express the hope that one day the authors will give us the English equivalent of Merck's "Reagenz-Verzeichnis"?

NORMAN EVERS