MAY, 1927. Vol. LII., No. 614.

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, 6th April, Mr. John White, F.I.C., Vice-President, being in the Chair.

Certificates were read for the first time in favour of Messrs. Frederick Cecil Bullock, B.Sc., A.I.C., Thomas Harold Fairbrother, M.Sc., F.I.C., Ralph Skinner Rack, and Samuel George Sherman.

Certificates were read for the second time in favour of Messrs. Alfred George James Lipscomb, B.Sc., A.I.C., William L. Matthews, Sydney John Rogers, B.Sc., F.I.C., Ernest Fred Waterhouse, Harold William Webb, Arthur Samuel Wood, M.Sc., Ph.D., F.I.C.

The following were elected Members of the Society:—William Gordon Carey, F.I.C., William Farrand Elvidge, B.Sc., A.I.C., Lewis Sidney Fraser, B.Sc., A.R.C.Sc., A.I.C., Frederick Percival Hornby, B.Sc., A.I.C., Gerald Roche Lynch, O.B.E., M.B., B.S., D.P.H., Eric C. Martin, and George Gilmour Philip.

The following papers were read and discussed:—"The Sequence of Strokes in Writing." By C. Ainsworth Mitchell, M.A., F.I.C., and T. J. Ward; (i) Some Observations on the Washing of Gluten from Flour," and (ii) "A Numerical Expression for the Colour of Flour," by D. W. Kent-Jones, Ph.D., B.Sc., F.I.C., and C. W. Herd, B.Sc., F.I.C.; and "The Determination of Free Mercury in Commercial Products," by H. B. Dunnicliff, M.A., Sc.D., F.I.C., and Kishen Lal, M.Sc.

On the Presence and Detection of Furfural in Vinegar.

By L. H. LAMPITT, D.Sc., F.I.C., E. B. HUGHES, M.Sc., F.I.C., and L. H. TRACE, B.Sc., A.I.C.

(*Read at the Meeting, December* 1, 1926.)

WHILST the sophistication of vinegar is not now carried out in the crude way adopted by manufacturers years ago, and whilst, as a consequence, the test for furfural has not the same significance it once had, nor the same importance as formerly, we have invariably, in the course of the routine testing of several hundreds of samples of vinegar, found a positive reaction with commercial distilled vinegars to the extent of ten to sixty parts of furfural in one million parts of vinegar. As furfural, according to Anderson,[15] is present neither in malt nor in wine vinegar (although cider vinegar may contain a trace), we have thought it of interest to carry out some experimental work in order to find an explanation of its presence in the distilled product, particularly as no direct reference could be found in chemical literature.

The following is a brief summary of the work, together with a description of a simplified test we have worked out.

I. THE ORIGIN OF FURFURAL IN DISTILLED VINEGAR.—It has been shown[27, 9, 4] that furfural is produced in wort during hopping, its formation being ascribed to the action of lactic acid on pentosans, and by various other workers that it is also produced in the distillation of wine, beer, strong solutions of sugar, pentosans and pentoses, gums, etc.,[1–8 and 10] and, therefore, in referring to the testing of worts for furfural, Nagel[9] recommends that, if the test is to be carried out on the distillate, only the first portion of this should be used, since the acid present in the wort is sufficient to convert the pentosans or pentoses present into furfural, the action proceeding with increasing intensity as the distillation progresses, owing to the increase in concentration of the acid. Consequently, as Nagel points out, only the first small portion of the distillate will be free from the furfural formed by distillation, but it will contain any furfural originally present as such in the liquid before distillation. Nagel further states that the formation of furfural may be prevented by previous neutralisation of the acid before distilling, and that similar considerations apply to wines and beers. Incidentally the test for furfural given by Leach[12] specifies that only the first few drops of distillate are to be tested.

Pasquero and Cappa[11] neutralise wines, spirits and beers before distilling, when a test for furfural is to be carried out, and French chemists generally[13, 14] apply the test to the distillate obtained from the neutralised vinegar. We have devised a test, described later, in which distillation is avoided.

It would appear from what has been said that the presence of furfural in distilled vinegar is due to acid hydrolysis of the pentosans and pentose bodies of the vinegars during the distillation, and this we have confirmed experimentally, and moreover have shown that furfural is not formed unless the vinegar is heated to 80° C. or higher. For example, vinegar was heated under a reflux condenser at various temperatures, and the furfural formed determined after a definite time. Some results are shown in Table I, where 5 per cent. acetic acid coloured with caramel was used as a check.

TABLE I.

Temperature.	Time of Heating.	Furfural in parts per million from: Malt vinegar (caramel free).	Furfural in parts per million from: 5 per cent. acetic acid (coloured with caramel).
	Before heating	Nil.	Very slight trace.
50°C.	3 hours	Nil	Less than 0·5
60°C.	3 hours	Nil	Less than 0·5
70°C.	3 hours	Nil	Less than 0·5
80°C.	3 hours	Slight trace	Less than 0·5
90°C.	3 hours	0·5	Less than 0·5
100°C.	3 hours	3·2	Less than 0·5
100°C.	3 hours	3·6	Less than 0·5
100°C.	6 hours	6·0	Less than 0·5

From these results it will be seen that vinegar gives rise to furfural only on heating above 80°C., the production at 100°C. being appreciable and increasing with time, whilst acetic acid with caramel under the same conditions shows no increase in furfural content. Vinegar concentrated *in vacuo* (below 70°C.) does not give rise to furfural, both the residue and the vapours giving no reaction for this aldehyde.

Table II gives results obtained on a manufacturing scale (experiment by courtesy of the manufacturers) in which 400 gallons of malt vinegar were submitted to ordinary commercial distillation, the process being stopped when 350 gallons had distilled over, 6½ hours after the commencement. The first few drops of distillate contained no furfural, but as distillation progressed, the amount of furfural passing over into the distillate increased.

TABLE II.

	Furfural: parts per million.
Original vinegar	None
Immediately boiling commenced	2·3
Distillate sampled at condenser mouth after distilling ½ hour	4·6
,, ,, ,, ,, ,, 1 ,,	6·4
,, ,, ,, ,, ,, 1½ ,,	7·4
,, ,, ,, ,, ,, 2 ,,	7·8
,, ,, ,, ,, ,, 3 ,,	8·3
,, ,, ,, ,, ,, 4 ,,	8·3
,, ,, ,, ,, ,, 5 ,,	8·7
,, ,, ,, ,, ,, 6 ,,	9·7
,, ,, ,, ,, ,, 6¼ ,,	9·7

Previous neutralisation of the vinegar resulted in a distillate free from furfural.

That the distillation on a commercial scale causes a considerable reduction in the pentosan content of the vinegar is shown by the following figures:—

TABLE III.

	Original vinegar, Per cent. W/V.	Residue in still, Per cent. W/V.
Total solids	2·10	9·70
Pentosans (calculated as furfural on original vinegar)	0·105	0·208
Pentosans (calculated as furfural on dry solids of vinegar)	·5·0	2·1

Pentosans in this experiment were determined by the A.O.A.C. hydrochloric acid hydrolysis method[17], the resulting furfural being determined by the following methods: (*a*) Kröber's phloroglucinol method[17]; (*b*) Ling and Nanji's phenylhydrazine method[18]; (*c*) the aniline acetate colorimetric method[16]. Incidentally, the comparison of the results obtained by these methods is shown in Table IIIA.

TABLE IIIA.

	Furfural in distillate from	
	Original vinegar. Per cent.	Residue in still. Per cent.
Kröber's method	0·109	—
Ling and Nanji's method ..	—	0·208
Aniline acetate method	0·102	0·209

Some of the malt from which this vinegar was prepared was ground up with water, warmed to 55°C. for a short time and filtered. The filtrate was tested for furfural, but gave a negative result. It was then acidified with acetic acid to 5 per cent. acidity (acetic) and distilled. Positive results for furfural were obtained with the distillate, the intensity of reaction increasing in the later fractions, thus indicating that acetic acid is capable of hydrolysing the soluble pentose bodies derived from the malt.

Distillation of a 5 per cent. acetic acid solution containing 0·2 per cent. of arabinose gave weakly positive tests for furfural in the first few fractions, gradually increasing in intensity in later fractions. The reactions obtained in this experiment were much less intense than those obtained by direct distillation of vinegar itself, but this is not surprising, as the source of furfural may probably not be arabinose, but another pentose body which is more readily hydrolysed than arabinose. This is stated by Haid[19] to be the case in wine.

The possibility of caramel being a source of furfural in coloured malt vinegar has been thoroughly investigated, and our results show that such a vinegar may contain a minute trace of furfural (about 0·5 part per million) which was previously present in the caramel, but that no formation of furfural from caramel by the distillation process takes place.

II. THE DETECTION AND DETERMINATION OF FURFURAL IN VINEGAR.—In testing for furfural, it is usual to employ the well-known aniline acetate reaction

which depends on the production of the rose-red colour of furfuraniline by the interaction of furfural and aniline acetate. (For the composition of furfuraniline and the reactions involving its formation see references[20,21,22,23,24]). This reaction can be considered as specific, not being given by other common aldehydes or ketones. We have found, however, that other organic acids, such as formic, propionic, butyric, valerianic, caprylic, tartaric, citric, lactic, can take the place of the acetic acid in the reaction. Of the mineral acids, only hydrochloric acid is really effective, and only at certain concentrations, the best colour being obtained with an amount of acid just sufficient to convert the aniline into the hydrochloride; the colour so obtained is deeper than when acetic acid is used and much more lasting. In place of aniline other simple aromatic primary amines may be used; for example, ortho- or paratoluidine and ortho- or para-xylidene give a colour of about the same intensity as that obtained when aniline is used; benzidine gives an intense crimson colour which develops rapidly but soon fades; the amino-sulphonic acids do not give the reaction, nor do secondary and tertiary amines. The intensity and stability of the colour depend on the particular combination of acid and amine used. The colour fades completely in 2 hours if exposed to light (in all cases tried except with hydrochloric acid and tartaric acid, where the fading times are 18 and 5½ hours respectively), but much less rapidly in the dark.

With a view to modifying the aniline acetate test (for our experiments have indicated that no practical advantage is to be gained by the use of any other combination) in order to make it applicable to dark-coloured products without distillation, we have investigated the solubility of the furfuraniline complex in various solvents.

The furfuraniline colouring substance is insoluble in petroleum spirit, carbon disulphide and in carbon tetrachloride. It is soluble, but with much diminished intensity of colour, in chloroform and in tetrachlorethane. Both benzene and ether dissolve the coloured product, but do not remove it completely from the reaction mixture, and when the furfural is present only in minute quantity a considerable proportion remains unextracted, as the following results show:—

TABLE IV.

Amount of furfural added to 20 ml. of 5 per cent. acetic acid. Mgrms.	Amount of furfural removed by three extractions with 20 ml. of ether. Mgrms.
5	4·5
2	2·0
0·5	0·4
0·1	Less than 0·05

Amyl alcohol, however, acts as a good solvent both as regards complete extraction and intensity of colour, and accordingly this solvent has been used.

DETERMINATION OF FURFURAL IN VINEGAR.—In the case of distilled vinegar or pale coloured vinegar it is sufficient to use the method of Youngburg and Pucher,[16] but for dark coloured vinegars (or other coloured products) the following

test which we have devised gives satisfactory results and has the important advantage of avoiding distillation.

Method.—Dissolve 6 ml. of redistilled aniline in 24 ml. of glacial acetic acid and make up to 60 ml. with pure amyl alcohol. (These reagents are completely miscible). Add 10 ml. of this mixture to 20 ml. of the vinegar or other product to be examined, shake thoroughly and then allow the mixture to stand in the dark for 15 minutes. Under these conditions the amyl alcohol separates as a distinct layer, coloured deep red if furfural is present. This test is capable of detecting 0·1 part of furfural in a million parts of very dark coloured vinegar, and the following table shows the degree of accuracy given by the method:—

TABLE V.

Amount of furfural added to 20 c.c. dark vinegar free from furfural.		Amount of furfural found.	
Mgrm.	Parts per million.	Mgrm.	Parts per million.
0·010	0·5	0·010	0·5
0·020	1·0	0·022	1·1
0·040	2·0	0·042	2·1
0·050	2·5	0·055	2·75
0·080	4·0	0·084	4·2
0·100	5·0	0·100	5·0

A sample of distilled vinegar gave results of 60 parts per million of furfural by this method and of 62 parts per million by Youngburg and Pucher's direct colorimetric method.

It may be mentioned that, coincident with the investigation, we thought it of interest to determine the alcohol content of various distilled vinegars. We found from 230 to 1260 parts of alcohol (w/v) per million parts of vinegar. A very convenient method for this determination is that of Martini and Nourrisson,[25] care being taken first to remove aldehydes by means of mercuric oxide.[26]

We wish to record our thanks to Messrs. Champion and Slee for the facilities offered us in carrying out the factory tests, and to Messrs. J. Lyons & Co., Ltd., in whose laboratories it was carried out, for permission to publish this work.

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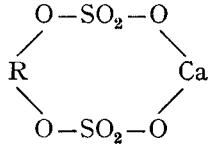
Irish Moss Mucilage and a Method for Its Determination.

By PAUL HAAS, D.Sc., and BARBARA RUSSELL-WELLS, Ph.D.

(*Read at the Meeting, February* 2, 1927.)

The substance known in commerce as Irish Moss is the sun-dried and bleached thallus of the red sea weed, *Chondrus crispus*, commonly called carrageen in Ireland. When the commercial product is soaked in water it swells up considerably, and, on warming, yields, according to the quantity of water employed, a more or less viscous solution known as Irish moss mucilage. It was shown some time ago (Haas and Hill, 1921) that even after prolonged dialysis such an aqueous extract of the sea weed retains ash constituents amounting to about 20 per cent, consisting chiefly of calcium sulphate; the dialysed mucilage was subsequently found to contain ionised calcium but no sulphate ion (Haas, 1921); on hydrolysis with hydrochloric acid, however, the sulphate was set free, thus proving the substance to be an ethereal sulphate of the type represented by the formula:—



in which R represents a carbohydrate complex.

A further study of the mucilage revealed the fact that it is actually a mixture of two substances which, while differing slightly in their chemical composition, are chiefly distinguished by their physical properties. One of these substances, known for convenience as the cold extract (C.E.) is soluble in cold water to form a viscous solution which does not set to a jelly on concentrating and cooling; the other, known as the hot extract (H.E.) is only sparingly soluble in cold water,

but dissolves in hot water to yield a solution which, unlike agar or gelatin, is viscous while hot, but on cooling sets to a gel if the concentration of the solution exceeds about two per cent.

PRECIPITATION WITH BENZIDINE.—In the course of a recent investigation on the hydrolysis of carrageen mucilage it became necessary to determine free sulphate in presence of unchanged mucilage, and recourse was had to the volumetric method involving the use of benzidine, when it was observed that a solution of benzidine chloride precipitated not only the free sulphate but the ethereal sulphate of carrageen as well. It is now shown that this precipitation may be utilised as a method for determining the amount of carrageen extract in solution.

The first point to be established was the fact that the precipitation by benzidine was specific for carrageen; for this purpose agar and a number of similar ethereal sulphates extracted from sea weeds were treated with benzidine chloride solution, and in no case was any precipitate formed; it was further shown that benzidine chloride does not precipitate solutions of gelatin, gum arabic or the pectins obtained from orange and apple, a fact of importance in connection with the possible application of the method to the determination of carrageen mucilage in jams, jellies, etc., or in adhesives.

It was next found that benzidine chloride solution, when added to either H.E. or C.E., effected in each case a quantitative precipitation, leaving the resulting solution free from carbohydrate. When warmed with water at 70°C. the precipitate formed from C.E. dissolved completely, but that formed from H.E. was only partly soluble.

TITRATION VALUES OF CARRAGEEN PRECIPITATES.—In order to obtain a measure of the amount of carrageen precipitated in this way the precipitate was filtered off, washed with saturated benzidine sulphate solution until free from chloride, suspended with its filter paper in water, the temperature raised to 80°C., and the liquid titrated with 0·1 *N* sodium hydroxide solution in presence of phenolphthalein. The following values were obtained as the equivalents of one grm. of H.E. and C.E. respectively:—

Precipitate from 1 grm. of H.E. required 29·2 c.c. of 0·1 *N* NaOH. (mean value) for neutralisation.

Precipitate from 1 grm. of C.E. required 32·6 c.c. of 0·1 *N* NaOH (mean value) for neutralisation.

Owing to the circumstance that both H.E. and C.E. are completely precipitated by benzidine chloride, and the fact that their solubilities in water are not sufficiently different to enable them to be separated by this means, it is not possible to determine the relative amounts of the two constituents in a mixture. In order, therefore, to obtain an expression for the correct value for the equivalent of 1 grm. of mixture, calculations were made for the various possible mixtures of the two substances, with the results shown in the following table:—

			H.E. Grm.	C.E. Grm.			0·1 *N*. NaOH. c.c.
1 grm.	of	mixture containing	0·1	0·9	would	require	32·26
,,	,,	,,	0·2	0·8	,,	,,	31·92
,,	,,	,,	0·3	0·7	,,	,,	31·58
,,	,,	,,	0·4	0·6	,,	,,	31·24
,,	,,	,,	0·5	0·5	,,	,,	30·90
,,	,,	,,	0·6	0·4	,,	,,	30·56
,,	,,	,,	0·7	0·3	,,	,,	30·22
,,	,,	,,	0·8	0·2	,,	,,	29·88
,,	,,	,,	0·9	0·1	,,	,,	29·54

This table shows that the titration value for carrageen mucilage is very slightly affected by the relative proportions of H.E. and C.E. in the mixture, and the mean value of 30·9 c.c. of 0·1 *N* sodium hydroxide solution may therefore safely be taken as being equivalent to one grm. of dry extract; or, otherwise expressed, 1 c.c. of 0·1 *N* NaOH = 0·0324 grm. of extract. In support of this view known amounts of oven-dried carrageen mucilage were dissolved in water, precipitated and titrated, and the amount present was determined by using the mean figure 0·0324, with the following result:—

Mixture (weighed) Grm.	Titration value 0·1*N* NaOH c.c.	Calculated amount of mixture. Grm.
0·20	6·55	0·212
0·17	6·15	0·199

A comparison of the calculated value with the amount of substance weighed out shows a sufficiently close agreement, more particularly as drying the mucilage to constant weight is a somewhat difficult process in view of the tendency of this substance to char at the temperature of the steam oven.

To check the accuracy of the determination of the end-point of the titration several different quantities of the same solution were precipitated and titrated, and, from the results given below, it is clear that the percentage of carrageen can be determined with a sufficient degree of accuracy to justify confidence in the reliability of the method.

Mixture used. c.c.	Titration value. 0·1*N* NaOH. c.c.	Carrageen found. Grm.	Carrageen found. Per cent. (W/V).
30	6·15	0·20	0·66
40	8·35	0·27	0·67
45	9·10	0·29	0·65

As a further example the following figures obtained for different weights of the same decoction of Irish moss, prepared according to the British Pharmaceutical Codex, may be quoted:—

Decoction. Grms.	Titration value. 0·1*N* NaOH. c.c.	Carrageen found. Grm.	Carrageen found. Per cent.
8·77	4·6	0·1489	1·70
8·82	4·7	0·1521	1·72

METHOD OF DETERMINATION.—In view of these facts, the following procedure is recommended for the determination of the mucilage. A quantity of the solution, containing approximately 0·2 grm. of dry extract, is either measured or weighed out, according to the viscosity of the fluid. The solution is then diluted to about 100 c.c., acidified with 4 drops of 4 *N* hydrochloric acid, and precipitated with 150 c.c. of benzidine chloride solution, containing 4 grms. of benzidine and 5 c.c. of concentrated hydrochloric acid in 2 litres. The mixture is allowed to stand for at least 20 minutes, and the flocculent precipitate is then filtered off through a fluted filter paper, and washed free from chloride with a saturated solution of benzidine sulphate. The precipitate and filter paper are put into a beaker, covered with about 250 c.c. of water, heated on a water bath to 80°C. and titrated with 0·1 *N* sodium hydroxide solution in presence of phenolphthalein. The amount of mucilage is calculated on the basis that 1 c.c. of 0·1 *N* sodium hydroxide solution corresponds to 0·0324 grm. of mucilage, as explained on p. 267. The whole operation can be completed in about 2 hours.

CARRAGEEN IN PRESENCE OF OTHER SUBSTANCES.—In order to see whether the mucilage could be determined in the presence of other viscous or colloidal substances, determinations were carried out in the presence of agar, gum arabic, gelatin and apple pectin. The results are appended.

	Mucilage taken. Grm.	Mucilage found. Grm.
Agar present in solution 0·025 grm. ..	0·171	0·178
Gum arabic present in solution 0·1 grm. ..	0·148	0·148
Pectin present in solution 0·1 grm. ..	0·148	0·148
Gelatin present in solution 0·1 grm. ..	0·148	0·149

The above substances were selected in view of the possible use of carrageen mucilage as an adulterant of jams, jellies and other commercial products.

APPLICATION TO COD LIVER OIL EMULSION.—As a further example of the use of the method, it was applied to the determination of mucilage in a cod liver oil emulsion kindly supplied by Dr. Hampshire of University College Hospital Pharmacy. The exact amount of mucilage added was not known, but, from the results obtained on determining the mount in various quantities of the emulsion, it may be seen that the method gives concordant results.

Emulsion used. c.c.	Titration value 0·1*N* NaOH. c.c.	Carrageen found. Grm.	Carrageen per 100 c.c. Grm.
20	3·4	0·1100	0·550
30	5·1	0·1650	0·550
37	6·0	0·1942	0·535

For this determination the presence of the oil necessitated the following modified procedure:—

The measured quantity of emulsion was made slightly acid with hydrochloric acid and precipitated with 150 c.c. of benzidine chloride solution for every 0·2 grm. of carrageen present ; it was then filtered through a fluted filter paper. and washed free from chloride with saturated benzidine sulphate solution. The filter paper

and precipitate were transferred to a beaker, sufficient chloroform added to dissolve out all the oil, and the whole then covered with about 250 c.c. of water, heated on the water bath until the chloroform began to boil, and titrated hot with 0·1 *N* sodium hydroxide solution in presence of phenolphthalein.

DETERMINATION IN PRESENCE OF FREE SULPHATE.—Experiments have been made with the view of ascertaining whether or not it is possible to determine carrageen extract in presence of free sulphate, although the likelihood of appreciable quantities of sulphate being present in carrageen mucilage is remote. The method consists in determining the carrageen extract by means of benzidine in a solution in which the free sulphate has been previously precipitated by barium chloride. It was found, however, that barium chloride precipitates carrageen extract to some extent and that the results of determination of mucilage in solutions to which barium chloride had been added were low. In solutions containing appreciable quantities of sulphate, however, the barium chloride appears to precipitate the sulphate in preference to the carrageen extract, with the result that an approximate determination of both carrageen and sulphate can be made in the same solution by precipitating the carrageen in the presence and in the absence of added barium chloride. It is necessary, however, to add a considerable excess of benzidine chloride to ensure complete precipitation of both the carrageen and the sulphate. The following figures give the results of such an experiment.—

(1) Forty c.c. of carrageen mucilage containing 0·1100 grm. of potassium sulphate, precipitated in the cold* with 0·8 grm. of barium chloride, followed by 150 c.c. of benzidine chloride, required 5·9 c.c. of 0·1 *N* sodium hydroxide solution; whence amount found was 0·1912 grm. of carrageen, whilst the amount added was 0·2009 grm. of H.E.

(2) Forty c.c. of the same solution, precipitated with 300 c.c. of benzidine chloride in the absence of barium chloride required 18·75 c.c. of 0·1 *N* sodium hydroxide solution deducting 5·9 c.c. from this figure, the amount of potassium sulphate found is (12·85 × 0·0087) = 0·1118grm. The amount added was 0·1100 grm.

SUMMARY.—(1) A method is described for determining the amount of Irish moss mucilage in solution, which depends upon the complete precipitation of the mucilage by benzidine chloride and titration of the filtered and washed precipitate, suspended in water, with 0·1 *N* sodium hydroxide solution, as for sulphates.

(2) The method can be employed in the presence of a number of other mucilaginous substances and should therefore be capable of application in the detection and determination of carrageen in jams, jellies or other substances.

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* This precipitation must be carried out in the cold in order to avoid hydrolysis of the carrageen.

The Determination of Soluble Iodides.

By J. F. SPENCER, D.Sc., Ph.D., F.I.C., and
M. LLEWELLYN SMITH, B.Sc., A.I.C.

Difficulty is frequently experienced in the determination of soluble iodides by Dietz and Margosches' method (*Chem. Ztg.* 1904, **2**, 1911).

The method consists in the addition of a measured excess of standard potassium iodate to the iodide solution in the presence of hydrochloric acid, when iodine is set free. Calcite is added to the solution, which is boiled until colourless. After cooling, potassium iodide is added, and the liberated iodine titrated with standard sodium thiosulphate solution, whereby the excess of iodate is determined. If by any means the hydrochloric acid becomes too concentrated it decomposes some of the excess iodate, giving iodine chloride, with the result that the amount of iodide found is too high.

A number of experiments have been carried out with the object of finding an acid which will allow of wide variations of concentration without affecting the undecomposed iodate. With acetic acid the reaction was found to be incomplete; the results being about 16 per cent. too low. Phosphoric acid gave entirely satisfactory results. It was found also that the iodine set free on the addition of iodate is expelled rapidly by merely boiling the solution; it is unnecessary to add calcite to aid the expulsion. On boiling the solution the iodine was removed and a colourless solution obtained in 10 minutes, whilst in the presence of calcite the expulsion required 7 minutes. The method, as modified, therefore consists in adding a measured excess of a standard potassium iodate solution to the solution of soluble iodide, which contains about 20 c.c. of an approximately 2 *N* solution of phosphoric acid. The mixture is then boiled until colourless, cooled, treated with 1 to 2 grms. of potassium iodide, and the liberated iodine titrated with standard sodium thiosulphate solution.

(i) *Acetic acid.*—A solution of potassium iodide containing 12·0220 grms. per litre was treated in 10 c.c. portions with 25 c.c. of 0·09516 *N* potassium iodate solution and about 20 c.c. of 10 per cent. acetic acid. After boiling off the iodine, potassium iodide was added, and the liberated iodine titrated with 0·09268 *N* sodium thiosulphate solution. According to the equation—

$$KIO_3 + 5KI + 6HA = 6KA + 3I_2 + 3H_2O$$

the amount of thiosulphate solution required is 16·3 c.c. It was found, as the mean of seven closely agreeing titrations, that 17·96 c.c. of thiosulphate were used. This figure indicates that the solution contained 0·0930 grm. of potassium iodide in 10 c.c., whilst the amount actually present was 0·1202 grm.

(ii) *Phosphoric acid.*—In this case 10 c.c. of a solution of potassium iodide containing 13·8842 grms. per litre were treated with 25 c.c. of a 0·09516 *N* solution

of potassium iodate and about 20 c.c. of 2 *N* phosphoric acid. The remainder of the determination was carried out as described above. Theoretically 14·83 c.c. of thiosulphate solution should be required for the titration, the mean of seven very closely agreeing titrations was 14·83 c.c. The experiments were repeated in the presence of calcite, when the same result was obtained.

DEPT. OF INORGANIC CHEMISTRY,
BEDFORD COLLEGE (UNIV. OF LONDON).

The Determination of Sulphur Dioxide in Dried Fruit.

BY PERCY MAY, D.Sc., F.I.C.

THE importance of the determination of sulphur dioxide or sulphites in foodstuffs at the present time needs no emphasis. Although no novelty is claimed for the method here described, it is hoped that its publication may help towards the achievement of greater uniformity in the results obtained by different analysts. Dried fruits form a convenient class of foodstuffs for the purpose of investigation, as they are free from sulphides or volatile sulphur compounds, and hence reliable blanks can be carried out with unsulphured fruit, and added sulphur dioxide can be determined under most favourable conditions.

It is unfortunate that, up to the present, it has not been possible to devise any simple volumetric method, and the only process giving satisfactory results is that of distillation of the sample with acid, with oxidation of the sulphur dioxide in the distillate and subsequent gravimetric determination of the sulphuric acid produced. This method in its general outlines is well known, but unfortunately considerable discrepancies have been observed in determinations on the same sample by different analysts. On the other hand, the details here given have been found to give results, not only consistent amongst themselves, but also usually rather higher than those obtained by other analysts. As will be shown later, all the likely errors tend to give low results, and therefore the higher result may be taken as *prima facie* evidence of accuracy, especially in view of the fact that a considerable number of blank experiments with unsulphured fruits have given consistent zero results.

SAMPLING.—Dried fruits may be divided into two categories with regard to the presence of sulphur dioxide:—

(1) Comparatively dry fruits in which 2000 parts of sulphur dioxide per million are allowed, including apricots, peaches, nectarines, apples and pears.

(2) Moister fruits in which only 750 parts per million are allowed, namely sultanas and raisins.

For a determination in a sample belonging to the first group, a fair sample of about 100 to 200 grms. of the fruit is minced in a machine, again well mixed, and 25 grms. weighed out for the determination, but for the second group it will be found more convenient to weigh about 40 grms. for the analysis, care being taken to get a good average sample, and then to cut the fruit in halves. For these moister fruits the use of a mincing machine is rather inconvenient, but it is important not to use whole fruit, as that may tend to give low results.

METHOD OF DETERMINATION.—In either case the weighed quantity of fruit is placed in a round-bottomed flask of about 500 c.c. capacity, containing 25 grms. of marble, and connected, by means of a splash-head, with a condenser fitted with an adapter dipping into 100 c.c. of saturated bromine water. Twenty-five c.c. of concentrated hydrochloric diluted to 300 c.c. with recently boiled distilled water are then run into a flask from a tap-funnel, and the apparatus left at room temperature until the evolution of carbon dioxide has slackened. The flask is then heated very gently until all the carbon dioxide has been evolved, and the flame then increased so as to keep as steady a distillation as possible until about 200 c.c. have distilled over. If the bromine should become decolorised, more bromine water should be added, but 100 c.c. are usually sufficient. The distillate is then evaporated down to about 120 c.c., and the barium sulphate precipitated and weighed with the usual precautions.

It is necessary to carry out a blank, but, with bromine and other chemicals of good quality, this should be zero. If there is a small positive blank, it is usually due to the bromine water, and in that case if more than 100 c.c. are used in an experiment, allowance must be made for the excess. For economy, when many determinations have to be made, bromine is preferable to iodine or hydrogen peroxide, and hydrochloric acid is preferable to phosphoric acid. Several blanks were made with unsulphured raisins and sultanas, and in no case was any barium sulphate at all precipitated under these conditions, showing that hydrochloric acid and bromine are free from objection, and that there is no danger of high results from their use. On the contrary, hydrochloric acid seems preferable to phosphoric acid, as it appears to cause a more rapid liberation of the sulphur dioxide from its compounds with sugar (*vide infra*).

SOURCES OF ERROR.—The following errors might be expected on general grounds.

Results too high.—(1) Splashing, causing traces of sulphate to appear in the distillate. (2) Reduction of sulphates in fruit by organic matter. (3) Sulphur in the chemicals. (4) Insufficient washing of the barium sulphate.

Results too low.—(1) Incomplete removal of sulphur dioxide from fruit. (2) Oxidation of sulphur dioxide before distillation. (3) Incomplete absorption of sulphur dioxide in the distillate. (4) Mechanical loss. The zero blanks show that the first three causes of possible high results have been eliminated, and special care has been taken to ensure thorough washing of the barium sulphate, and it may therefore be assumed that incorrectly high results cannot be obtained with reasonably careful working.

There is, however, some risk of low results, and, from the nature of the case, it is almost impossible to prove directly whether this danger has been overcome. The sulphur dioxide is absorbed in the fruit by exposing it to the gases from burning sulphur, and it is probably mostly in combination with the sugars of the fruit. Test experiments, in which aqueous sulphite solutions of known strength are added to the dried fruit before determination, are therefore not very convincing, but, as far as they go, they confirm the accuracy of the method. More importance may be attached to the fact that admirable agreement has always been obtained in duplicate determinations, including those in which other and more elaborate precautions have been taken, and that results obtained by other workers with the same sample have never been more than 10 parts per million higher than those obtained in this laboratory, though in some cases they have been very considerably lower.

For example, a sample of sultanas analysed in this laboratory was found to contain 900 parts per million of sulphur dioxide, and the same sample examined by two other competent analysts was reported as containing 850 and 722 parts of sulphur dioxide per million respectively. These lower results may be due to the use of phosphoric acid instead of hydrochloric acid and consequent incomplete liberation of the sulphur dioxide from its sugar compounds.

It does not seem to matter materially whether corks or india-rubber stoppers are used in the experiments, provided that they make the apparatus gas-tight and are well seasoned and steamed before use. It is possible that new corks may absorb sulphur dioxide, as suggested by Parkes (ANALYST, **1926**, **51**), but no absorption has been noticed with corks which have been in use for some time. India-rubber stoppers, on the other hand, if new or dirty, may give off appreciable amounts of sulphur, and it is therefore important that they should be boiled with dilute soda solution, and then well steamed before use.

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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.

FEEDING EXPERIMENTS WITH CORN COCKLE

(*Agrostemma Githago, L.*).

PRIOR to 1921 a number of cases of alleged poisoning of pigs by corn cockle contained in millers' offals ("sharps" or "thirds") caused litigation, and claims for damages were made against the vendors on the strength of analyses certifying that the offals contained corn cockle in minute quantities.

In 1921 a claim was made by an owner of pigs in North Wales in which it was alleged that a proportion of 0·15 per cent. of corn cockle in certain "thirds" sold to him was responsible for the death of a number of his pigs. The title of the action was *Wm. Brumby* v. *E. B. Jones & Co., Ltd.*, the plaintiff being the owner of the pigs alleged to have died from corn cockle poisoning, and the defendant company being the proprietors of the stores from which the "thirds" in question had been bought. The action was heard at Liverpool on the 25th and 26th June, 1922, by Mr. Justice Swift, without a jury, the defendant company being represented by Mr. A. T. Miller, K.C., and Mr. A. T. Crosthwaite (instructed by Messrs. Wilson, Cowie & Dillon, solicitors). The millers who supplied the "thirds" which were sold to the claimant, being satisfied on *prima facie* evidence that such small quantities of corn cockle in "thirds" could not have been the cause of death of the pigs, determined to put the matter to direct test by feeding pigs under carefully controlled conditions on foods containing known, but varying, quantities of corn cockle purposely added.

Accordingly, I was approached, and, after discussion, it was arranged that Mr. Stafford Jackson, M.R.C.V.S., Lecturer in Clinical Veterinary Medicine and Surgery at the University of Liverpool, and I should carry out experiments in co-operation with Dr. Bernard Dyer.

For the purposes of experiment a litter of ten pigs from a sow of the Middle White variety belonging to Mr. James Lister, an extensive breeder of pigs, at Knotty Ash, near Liverpool, was selected, six of the litter having known quantities of corn cockle added to their rations, and the remaining four being fed precisely as the others, but without any addition of corn cockle.

The corn cockle used in the experiments was hand-picked from cockle screenings from the same classes of wheat as were used in the manufacture of the "thirds" of which complaints were made.

Each day during the experiments, which started on June 27th, and ended on 26th July, 1921, I examined the cockle seed used, to satisfy myself that it consisted wholly of corn cockle, and after it had been ground through the laboratory mills I weighed out in packages the quantities summarised in the table given below.

Mr. Stafford Jackson and I were present at Mr. Lister's piggery each day, except Sundays, and saw the corn cockle administered and eaten. On Sundays the pigman gave the alloted quantities to the various styes.

Mr. Stafford Jackson also took the temperatures of all the pigs fed on corn cockle on every visit. Except on two occasions, when the gilts were on heat and registered a temperature of 103°F., the whole of the figures obtained during the thirty days of the experiments ranged between 102° and 102·4°F., the normal temperature for pigs.

The following table gives the quantity of cockle consumed and the distribution of the pigs in the various sties:—

Ten Middle White pigs of 16 weeks old.		Quantity of corn cockle per pig per day. (Whole seed ground).	Quantity of food per pig per day.			Proportion of cockle seed to total food.	
Sty No.		Grains.	Millers' offals. lbs.	Other food. lbs.	Total. lbs.	Per cent.	= Grains per lb.
1	1 hog 2 gilts	168	4	4	8	0·30	21
2	1 hog	84	4	4	8	0·15	10·5
3	1 gilt	336	4	4	8	0·60	42
4	1 gilt	504	4	4	8	0·90	63
5	1 hog 3 gilts	Nil	4	4	8	Nil	

During the whole of the time of the feeding experiments the cockle-fed pigs throve exceedingly, and no difference between the pigs in the various sties could be observed on inspection. The final weights, taken on July 26th, 1921, showed that, in fact, the cockle-fed pigs had gained slightly more weight than the pigs in No. 5 sty which had received no corn cockle.

The pigs were then killed, and on July 29th, Mr. Stafford Jackson, Mr. Wynne, M.R.C.V.S., of Denbigh (on behalf of the plaintiff in the case) and I visited the farm at Knotty Ash, and the two former made a *post-mortem* on the gilt from No. 4 sty (that receiving the largest quantity of corn cockle), and also on a gilt from No. 5 sty which had received no corn cockle. All the internal organs of both pigs were found to be in a perfectly healthy condition, with the exception that the mucous membrane lining of the stomach of the gilt from No. 4 sty was perhaps slightly thickened and the villus portion slightly discoloured, but not enough to cause any irritation or any constitutional disturbance.

Both of the carcases were subsequently passed by the meat inspectors of the Liverpool Corporation Health Committee for use as human food.

At the trial of the case these experiments were recited in detail, and, after this and other evidence directed to the elucidation of the poisonous effects of corn cockle on animals generally, and of pigs in particular, Mr. Justice Swift, in giving judgment for the defendants, said, "I am not satisfied that the amount of corn cockle seed in the 'thirds' sold to plaintiffs contained a sufficient quantity of saponin to cause the death of the pigs."

My object in writing this résumé of the experiments is that the case was not adequately reported at the time, and it has come to my knowledge that some analysts are still under the impression that the oft-repeated statements in various text books, as to the poisonous effects of corn cockle seed, would justify them in condemning samples of offals containing minute and perfectly innocuous quantities of corn cockle.

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THE GELATIN PRECIPITATION TEST FOR TANNINS.

TANNING consists in the fixation of tannin by animal fibre, which property is demonstrated by the "Gold-beaters' Skin Test for Tannins," elaborated in this Laboratory by Atkinson and Hazleton (*Biochem. J.*, 1922, **16**, 516) and by Price, Colborn and Smyth (ANALYST, 1924, **49**, 25). This test has since been used by Hardy and Worneford (*Ind. Eng. Chem.*, 1925, **17**, 49) and Jordan and Ware (*Pharm. Jour.*, 1924, **113**, 102) who have reported favourably on it. In view of these considerations, the negative behaviour of Fischer's pentagalloylglucose towards the gold-beaters' skin test, although it precipitates gelatin (Nierenstein, ANALYST, 1925, **50**, 604), seemed to indicate that this substance is not a tannin and that the gelatin precipitation is not a specific test for the tanning properties of a substance, especially since it is stated in the literature that gum arabic (Pelletier, *Ann. Chim.*, 1813, **87**, 106), starch (Tollens, *Handb. d. Kohlenhydrate*, 1914, p. 525), inulin (Tollens, *ibid.*, p. 551) and methyl gallate (Nierenstein, *Ber.*, 1912, **45**, 837), all of which are not tannins, are also precipitated by gelatin. I have therefore tested the behaviour of 73 substances (non-tannins) towards gelatin and I have found 18 of them to give positive reactions.

The gelatin solution was prepared according to Grasser (*Handb. für Gerbereichem. Labor.*, 1922, p. 273). The following substances gave positive results:

(1) In 1 per cent. solutions: gallic acid, β-resorcylic acid, haematoxylin, brazilin, picric acid, ethyl gallate, *m*-hydroxybenzoic acid, hydroxyhydroquinone and maclurin; (2) Only in saturated solutions: phenol, resorcinol, catechol, phloroglucinol, pyrogallol, methyl gallate, guaiacol and protocatechuic acid.

Among those substances which did not give a positive reaction are gum arabic, starch and inulin, referred to above, and also catechin. According to Freudenberg (*Ber.*, 1920, **53**, 236; 1922, **55**, 1734, 1940) catechin is precipitated by gelatin, but this was not confirmed by Nierenstein (*J. Chem. Soc.*, 1922, **121**, 26; *Ber.*, 1922, **55**, 3832). In agreement with Nierenstein (ANALYST, 1923, **48**, 542), I find that *pure* catechin does not give a precipitate with gelatin, whereas impure catechin or pure catechin which had been heated in an aqueous solution for some time (about 60 minutes) is precipitated by gelatin.

From these observations it is evident that a positive gelatin test is no specific indication of the presence of a tannin.

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THE DETERMINATION OF CARBON DIOXIDE IN CARBONATES.

IN reply to the comments of Messrs. Back, Trace and Harvey (ANALYST, 1927, 77), on my paper, I wish to state that I was not aware of Mr. Van Slyke's previous work. My references (up to 1919) were drawn from Treadwell's *Analytical Chemistry*, 5th edition, and those subsequent to 1919 from the Chemical Society's Abstracts. With reference to Mr. Back's comments, I wish to point out that the "correct" result obtained after 20 minutes is probably a coincidence produced by two compensating errors. I have found by repeated experiment, that the absorption of carbon dioxide by 0·1 *N* baryta solution is not complete after so short a period as 20 minutes. On the other hand, as I have shown in the paper, the result obtained by back titration with hydrochloric acid is high. These facts are sufficient to account for the apparent accuracy of the results obtained by Mr. Back, in spite of the incomplete absorption. In this connection it is interesting to note that Mr. Callan in applying my modification of the method to the determination of sodium carbonate in dyestuffs (ANALYST, 1927, 222) finds that 6 hours are required for the complete absorption.

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Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods.

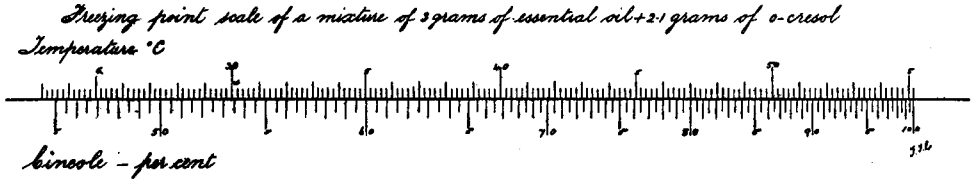
THE ESTIMATION OF CINEOLE IN ESSENTIAL OILS.

(I) CAJUPUT AND EUCALYPTUS OILS.

THIS Committee has found that the phosphoric acid process, as described in the British Pharmacopoeia, is unreliable, as shown by the actual results obtained by various members of this sub-committee on three test mixtures of known cineole content. These results are given in Table IA.

The Committee recognises that this process must be used in commerce so long as it is official in the Pharmacopoeia, but strongly recommends its omission in the next edition and its substitution by the ortho-cresol method.

The ortho-cresol method consists in determining the freezing point of a mixture of 3 grms. of the oil, previously dried by shaking with a little dry granular calcium chloride, and 2.1 grms. of ortho-cresol. The percentage of cineole is obtained from a scale prepared from the freezing points of ortho-cresol with mixtures of known cineole content.



The test is carried out in a stout-walled test tube, about 15 mm. in diameter and 80 mm. in length, fitted with a wire loop for suspending it from the stirrup of a balance. Three grms. of the oil and 2·1 grms. of melted ortho-cresol are weighed successively into the tube, finely drawn-out pipettes being used to introduce the liquids and the weighings carried out to an accuracy of one small drop from the pipettes, that is, to about 0·02 grm. or less than 1 per cent.

An accurate thermometer, graduated in *fifths of a degree*, is inserted, the mixture well stirred to induce crystallisation, and the highest reading of the thermometer noted. The tube is then warmed gently until the contents are completely melted, inserted through a bored cork into a wide-mouthed bottle to act as an air jacket, and allowed to cool slowly until crystallisation commences or the thermometer has fallen to the previously noted temperature. It is then stirred vigorously with the thermometer, the latter being rubbed on the side of the test tube with an up and down motion to induce rapid crystallisation, the stirring and rubbing being continued as long as the temperature rises. *The highest point is taken as the freezing point.* The mixture should be remelted and the test repeated until two concordant results are obtained, as the first temperature noted is always lower than the true freezing point. Corrections for emergent column are unnecessary, as any error thereby introduced is so small as to be negligible. Differences in the size of the thermometer bulb do not cause any variation in the freezing points recorded.

With oils of low cineole content, it may be necessary to introduce a minute crystal of the ortho-cresol-cineole addition compound,* to start crystallisation.

This method is satisfactory for oils containing 50 per cent. and upwards of cineole. Oils containing less than 50 per cent. may be mixed with an equal weight of pure cineole or a high-content oil before carrying out the test. A better way, however, is to perform the test in the usual manner first, and then, if the mixed liquids do not crystallise, add an equal weight (5·1 grms.) of pure recrystallised ortho-cresol-cineole compound,* warm until liquified, determine the freezing point as before, and make the necessary corrections.

* The pure ortho-cresol-cineole compound may be prepared from a high percentage oil by mixing with ortho-cresol, cooling, draining and pressing the crystalline magma, and recrystallising from a small quantity of petroleum spirit. The freezing point of this compound should not be below 55·2°C.

From the following table of freezing points the intermediate figures may be obtained by interpolation, or the result may be read from the appended scale.

Freezing point of 3 grms. oil + 2·1 grms. *o*-Cresol. °C.	Cineole by weight. Per Cent.	Freezing point. °C.	Cineole by weight. Per Cent.
24	45·6	40·4	67·5
25	46·9	41	68·65
26	48·2	42	70·5
27	49·5	43	72·35
27·4	50·0	44	74·2
28	50·8	45	76·1
29	52·1	45·2	76·5
30	53·4	46	78·0
31	54·7	47	80·0
32	56·0	48	82·1
33	57·3	48·4	83·0
34	58·6	49	84·2
35	59·9	50	86·3
36	61·2	51	88·8
37	62·5	52	91·3
38	63·8	53	93·8
39	65·25	54	96·3
39·8	66·5	54·6	98·0
40	66·8	55	99·3
—	—	55·2	100·0

These figures represent the mean values obtained experimentally on mixtures of known cineole content, and have been confirmed at three points by all members of this committee; the actual results being shown in the annexed table. The experimental error should not exceed ± 1 per cent.

It is important that the ortho-cresol should be pure and dry, with a freezing point not below 30°C., and, as it is hygroscopic, it should be stored in small well stoppered bottles as the presence of moisture may lower the results, even to the extent of 5 per cent.

TABLE (I)

	A Cineole Per Cent.	*B* Cineole Per Cent.	*C* Cineole Per Cent.
1.	49·6	70·0	88·2
	50·1	70·0	88·2
	50·1	70·25	88·5
	50·25	—	—
2.	48·9	71·5	88·2
	48·9	71·7	—
3.	49·5	70·5	87·8
	—	70·9	—
4.	49·9	71·1	88·2
5.	49·9	71·5	87·3
	50·8	71·7	87·5
	—	71·9	88·0
6.	50·4	71·5	88·2
7.	50·8	71·5	89·3
8.	50·25	71·0	88·5
9.	50·5	71·6	88·5
10.	49·5	70·2	88·5
11.	49·9	—	—
Mean	49·94	71·05	88·14
Maximum Variation	1·9	1·9	2·0
Actual Content	50	71·1	88·1

Table (I) shows the results of three mixtures of pure cineole, terpene and sesquiterpene circulated to all members for the purpose of confirming the accuracy of the scale, and Table Ia the results of the same mixtures by the phosphoric acid method.

TABLE (Ia).

Results by the Phosphoric Acid Method of the three Mixtures of known Cineole Content.

Member.	*A* Cineole Per Cent.	*B* Cineole Per Cent.	*C* Cineole Per Cent.
No. 1	46	63	92
„ 2	34	68	88
	36	—	—
„ 3	33	55	78
„ 5	46	69	87
„ 9	33	—	84·5
„ 10	44	77	90
Actual Content	50	71·1	88·1

Table (II) shows the results of four natural oils circulated to all members.

TABLE (II).

Cineole, Per Cent.

	Eucalyptus oil.			Cajuput oil.
	Australian No. 1.	Australian No. 2.	Spanish	
1	87·8	76·2	70·1	57·3
	87·8	77·1	70·5	57·3
	—	77·1	70·5	—
2	87·3	76·0	71·3	56·8
	87·0	76·2	71·0	57·0
3	87·5	76·5	70·0	57·5
	—	—	71·5	57·2
4	87·5	77·4	70·5	56·7
	87·6	77·4	71·0	57·0
5	88·1	77·4	71·6	58·3
6	87·0	76·7	69·9	58·0
	87·0	76·6	69·9	57·6
7	87·5	76·5	70·7	57·5
8	87·3	76·8	70·0	57·6
9	87·5	77·0	69·5	57·5
10	87·5	76·85	70·87	58·0
11	87·8	77·1	70·5	57·3
Maximum Variation	1·1	1·4	2·1	1·6

(*Signed*) John Allan (Chairman), C. T. Bennett, S. W. Bradley E. Theodore Brewis, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, C. Edward Sage, M. S. Salamon, W. H. Simmons, T. Tusting Cocking (Honorary Secretary).

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.

ANNUAL REPORT OF THE CITY ANALYST FOR 1926.

THE total number of samples examined under the Food and Drugs Acts was 4,820, of which 4,648 were informal and 172 formal samples. There were 158 adulterated samples and 34 label offences.

PRESERVATIVES.—Twelve samples were adulterated with preservatives. Sixteen of 22 samples of cake were either free from preservatives or contained only a small amount, but 5 samples of Genoa cake contained from 6 to 9 grains of boric acid per lb., and one sample of plain cake contained 17 grains per lb. One of the 22 samples of sponge cake contained 13 grains of boric acid per lb., but a subsequent sample from the same vendor was free from preservative. In 1921, when the first samples of sponge cake were taken, 71 per cent. of them contained boric acid.

MILK.—Of the 2659 samples analysed, 104 were adulterated.

In a few cases, milk somewhat below the 8·5 per cent. limit may be shown to be genuine, but, on the other hand, when the farm sample contains more than that proportion of solids-not-fat, milk, which by the presumptive limit would appear to be genuine, is shown to contain added water by comparison with the actual milk yielded at the farm. In these conditions it is very important that information should be obtained as to the fluctuation in the proportion of solids-not-fat from day to day in a herd of cows. For a number of years, series of samples have been taken from farmers whose milk showed large fluctuations of solids-not-fat, and it has been found that this variation practically ceased as soon as the farmers knew that samples of milk were being taken for analysis. The fluctuations were, therefore, not due to the cows, but to the variation in the amount of added water present. (*See* ANALYST, 1927, 78.)

MUSTARD.—Eighty samples were passed as genuine, though three, probably from one maker, were coloured with turmeric. This is unusual, turmeric generally being added to give colour to mixtures of mustard and starch.

SPIRITS.—Of 18 samples of whisky examined, 3 were adulterated, the amount of water being 2 per cent., 5 per cent. and 5 per cent. in excess of the legal limit. The vendor attributed the deficiency of alcohol to evaporation, but experiments to ascertain the rate of evaporation of Scotch whisky showed that, to produce an appreciable loss of strength there must be gross carelessness in keeping the whisky, and that, under reasonable conditions, evaporation will not account for the presence of 5 per cent. of excess water. Only when the experimental bottle had been left uncorked for 12 weeks was there any indication of excess water, and then only 1·4 per cent. (*See* ANALYST, **1926, 51**, 347.)

OINTMENTS. The B.P. requires that *boric acid ointment* shall contain 10 per cent. of boric acid. Nine samples contained from 9·7 to 10·8 per cent., and were passed as genuine; the vendors of two samples which contained only 8·4 and 8·7 per cent. were cautioned. Eight samples of *white precipitate ointment* contained from 4·5 to 5·0 per cent. of pure white precipitate, and were passed as

being in reasonable agreement with the requirements of the B.P. Eight samples of *zinc ointment* contained from 14·3 to 15·9 per cent. of oxide of zinc, the proportion required by the B.P. being 15 per cent. *See* also "Quarterly Reports" (ANALYST, 1926, **51**, 346, 512; 1927, 77, 223).

J. F. LIVERSEEGE.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

RICE FLOUR IN SHREDDED SUET.

ON February 25, the Potteries Stipendiary Magistrate (Mr. B. C. Brough) heard a case at Stoke-on-Trent, in which a manufacturing firm was summoned for selling shredded beef suet adulterated with ground rice.

Mr. J. M. Dodds, for the prosecution, said that the facts were similar to those in three other cases in which the magistrate had reserved judgment. A sample of suet sold by the defendants was found, on analysis, to contain 22.2 per cent. of ground rice, and it should also be mentioned that a sample from the same packet, when analysed at the Government Laboratory, was found to contain 15·52 per cent., so that the average amount present would be somewhere between these two figures. The contention of the Stoke-on-Trent authority was that anything in excess of 15 per cent. was more than was essential, and was to the prejudice of the purchaser.

Mr. E. V. Jones, Public Analyst for the County of Stafford, said that since 1923 he had analysed 60 samples, and these contained on the average 15·0 per cent. of added rice flour. The average amount in 24 samples of unknown origin was 15·38 per cent. In his opinion 15 per cent. should be regarded as a reasonable standard. The difference between his result and that of the Government Laboratory was due to the division of the packet made by the inspector.

Mr. W. T. Rigby, Public Analyst for Warwickshire, said that he had analysed samples of shredded suet made by ten different firms; of these, three contained more than 20 per cent. of ground rice, whilst the other seven contained 15 per cent. or less. He considered 15 per cent. a liberal allowance to make and cited instances within his experience in which the amount was as low as 8 per cent. In cross-examination, he said that he was unable to state whether the samples containing such low percentages also contained beef stearine.

Mr. Williams, for the defence, pointed out that the exact amount of rice flour added by his clients was 18 per cent., and even that quantity was not sufficient to prevent clogging in hot weather. He called a representative of the defendants to prove that it was impossible to regulate the percentage of rice flour in each packet.

On March 18, the Stipendiary gave his reserved judgment in this and the other cases. He said that it was conceded that the rice flour was not injurious to health, and that it was also conceded that some rice flour was necessary if the shredded fragments of suet were to remain separate. Sec. 6 (1) of the Food and Drugs Act applied when the ingredient added was required for the production or preparation of a food or drug as an article of commerce. As regards section 8 it might be worth while to take the opinion of the High Court on a case stated, whether

where a standard of quantity had, in the absence of a statutory standard, been fixed by a Court of trial, and that standard had been substantially exceeded, the manufacturer was still protected (in the case of a non-injurious ingredient) by a label given in accordance with the section.

The first thing that struck one on examining the results of analyses was the extraordinary variations in the quantities of rice flour present. In some cases it was as little as 6 per cent., and in others over 26 per cent. In the four cases before him the amounts varied from 15·52 to 22·2 per cent. One of the defendant firms had stated that they worked to an average of about 15 per cent. of rice flour, but he (the magistrate) did not know whether 15 per cent. of dry or desiccated rice flour or 15 per cent. of ordinary rice flour was meant; but the difference was essential. The percentages ascertained and certified by the Public Analyst referred to desiccated flour, and any standard fixed by the Court of trial should also be for desiccated and not ordinary rice flour. That gave a freer hand to the manufacturer, and when the percentage of the moisture present in commercial or ordinary rice flour was added to the permitted percentage of desiccated rice flour the total percentage of the two would be nearly, or quite as large as was asked for by the manufacturers. He thought that a standard of 15 per cent. was sufficiently high, but suggested that, in view of the difficulties in the way of securing the absolutely uniform distribution of the flour among and upon the shreds, food inspectors should not trouble about relatively small percentages over and above that standard.

He had not previously fixed a standard, and therefore considered that the fairest course in all these cases was to state that standard, with the suggestion he had made, and to dismiss the four summonses without making any order as to costs, except that the expenses of the Government analysis must fall upon the prosecution.

PEPPERMINT ESSENCE.

On March 11, a provision merchant was summoned at Sunderland for having sold peppermint essence which was not of the nature, substance and quality demanded.

The solicitor for the prosecution stated that the inspector had asked for six bottles of peppermint essence, which were supplied at the price of 7½d. per bottle.

According to the Public Analyst's report, the sample consisted of 0·3 per cent. of oil of peppermint, 1·81 per cent. of alcohol, and 98·16 per cent. of water; whereas, according to the *British Pharmacopoeia*, it should have consisted of 10 per cent. of oil of peppermint and the remainder of alcohol.

The inspector, in cross-examination, said that he did not expect to get spirit of peppermint, the cost of a similar bottle of which would have been about 2s. 6d. He did not know whether peppermint essence was in the *British Pharmacopoeia*.

The solicitor for the prosecution observed that the analyst's view was that spirit of peppermint was synonymous with essence of peppermint.*

The solicitor for the defence said that he disputed this statement of the Public Analyst. The essence was not in the *Pharmacopoeia*, and there was a distinct difference between it and spirit of peppermint, and there was no standard whatever for the essence. It was quite fair to say that the inspector could not reasonably expect to get spirit of peppermint for 7½d. per bottle. Before the purchase was made the defendant had mentioned that it was essence.

The bench dismissed the case.

* *Note :—The Brit. Pharm. Codex* says (p. 707) "Spirit of peppermint. *Syn.* Essence of peppermint."—EDITOR.

RASPBERRY JAM DEFICIENT IN RASPBERRY FRUIT.

ON March 10, a firm of grocers was summoned at Derry for the sale of raspberry jam which was deficient in raspberry fruit to the extent of at least 80 per cent. of the amount which should have been present.

Sir H. Miller, for the Corporation, said that the analyst's certificate stated that the sample contained 0·52 per cent. of raspberry fruit fibre, whereas genuine raspberry jam contained at least 3 per cent. of fibre from raspberry fruit.

For the defence it was stated that the bottle was labelled "Preserved Raspberry," and the assistant had been instructed to sell it under that name and not as jam. It was principally sold to the poorer classes.

The magistrates, by a majority, convicted and imposed a fine of £10, with £1 costs.

SUGAR DERMATITIS.

ON March 21, a workman applied in Bow County Court for the continuation of compensation from a firm of sugar refiners.

The applicant was certified on June 2, 1926, as suffering from an industrial disease, sugar dermatitis, and was paid compensation for total incapacity at 30s. a week up to October 26. Mr. Gorst, for the applicant, said that a peculiarity about the disease was, that it began at the tips of the fingers and went as far as the wrists, but no further, and from the toes, and went no further than the ankles.

Medical evidence was given that it would be dangerous for the man to work, as some of the patches might become septic. The case was typical of sugar dermatitis, in that it would flare up and go down intermittently; it would ultimately clear up, so long as the man did not go near sugar.

Judge Snagge awarded 13s. 6d. a week compensation, dating back to October, his judgment being based upon the fact that at times the man could work and that at times he could not.

BLACK CURRANT AND ORANGE AND QUININE WINES.

ON March 16, a man, trading as a company, was summoned at the Mortlake Police Court for selling black currant wine and orange and quinine wine not of the nature, substance and quality demanded by the purchaser.

According to the report of the Public Analyst for Surrey (Mr. E. Hinks) the black currant wine was an artificially coloured and flavoured solution of sugar acidified with a small proportion of organic acid. There was no definite evidence of the presence of black currant or other fruit juice. The proportion of quinine in the orange and quinine wine was only one-seventh of that contained in quinine wine prepared according to the *British Pharmacopoeia.*

A representative of a firm of essence manufacturers said that the defendant bought black currant essences from his firm, and that these contained a proportion of the fruit juice.

The solicitor for the defence pointed out that although the bottle was labelled "fruit wine," there was a further label marked "black currant flavour."

The Bench fined the defendants £10 with 10 guineas costs. They suggested that the summons for the orange wine should be withdrawn, and to this the prosecution agreed.

Ministry of Health.

OCCURRENCE OF GLASS FRAGMENTS IN FOODS PACKED IN GLASS CONTAINERS.*

GLASS containers are not regarded as objectionable as receptacles for food, for although glass in powdered or microscopic form is found in a very large number of foods, it is not only in those packed in glass containers, and there is little or no evidence of such minute particles exerting any injurious effect. Its source in this state is regarded as usually extraneous, often the dust of the factory or road dust. Soft fruits, for example, are often dusty when picked and, as a rule, are subjected to no washing process before boiling. Silicious particles are also contained in such dusts and may be differentiated from glass under the polarising microscope, and a series of typical photomicrographs is given for comparative purposes.

The suggestion that microscopic glass particles may be derived from the insides of the containers by flaking is not regarded as at all a likely or common source of contamination. Larger particles, of appreciable size, are but seldom found in foods packed in glass containers, but may arise from such causes as the use of jars with chipped or jagged rims, or failure to observe precautions when subjecting vessels to sudden changes of temperature by acclimatising, either by pre-heating or cooling the jam, etc. to a suitable temperature before filling, and also in retorting operations by failing to raise the temperature sufficiently gradually. Very few accidents due to these causes arise in present day practice, the average breakage during retorting being, in the case of one firm, for 1922, 0·11 per cent.; 1923, 0·11; 1924, 0·069; 1925 (first quarter), 0·059 per cent.

The method adopted by Dr. Monier-Williams (Ministry of Health) for the isolation of mineral residue from foodstuffs is to boil the material with 10 per cent. sulphuric acid in a Jena or Duro glass flask for about 30 minutes, to filter hot, with the aid of suction, through an ashless paper, wash the residue, return the residue and paper to the flask, boil with concentrated sulphuric acid, with repeated additions of small amounts of nitric acid, cool, dilute, centrifuge, wash the residue and treat it alternately with hot 10 per cent sodium hydroxide solution and concentrated hydrochloric acid, and finally to wash with distilled water, dry and weigh. The material is then mounted in glycerin jelly and examined in polarised light.

Blank experiments upon a filtered solution of pure cane sugar never showed any particles large enough to be identified as glass derived from the glass vessels used, and, in general, particles under 0·2 mm. in diameter are not to be regarded as proved to be glass. (*Cf.* ANALYST, 1925, **50**, 393; 1926, **51**, 626.)

D. G. H.

* *Reports on Public Health and Medical Subjects*, No. 37. By Dr. G. L. Hancock. Pp. 36. H.M. Stationery Office, 1927. Price 1s. net. With 15 plates.

PROVISIONAL RULES AND ORDERS, 1927.

PUBLIC HEALTH, ENGLAND.

PROVISIONAL REGULATIONS, DATED APRIL 8, 1927, MADE BY THE MINISTER OF HEALTH FOR AMENDING THE PUBLIC HEALTH (PRESERVATIVES, &c., IN FOOD) REGULATIONS.

71,855.*

The Minister of Health certifies under Section 2 of the Rules Publication Act, 1893, that on account of urgency the following Regulations should come into immediate operation and, in the exercise of the powers conferred upon him by the Public Health Act, 1875, (a) the Public Health (London) Act, 1891, (b) the Public Health Act, 1896, (c) the Public Health (Regulations as to Food) Act, 1907,(d) and the Butter and Margarine Act, 1907,(e) and of every other power enabling him in that behalf, hereby makes the following Regulations, with the consent of the Commissioners of Customs and Excise, so far as they apply to the Officers of Customs and Excise, to come into operation forthwith as Provisional Regulations that is to say:—

1. These Regulations may be cited as the Public Health (Preservatives, etc., in Food) Amendment Regulations, 1927; and these Regulations and the Public Health (Preservatives, etc., in Food) Regulations, 1925 (hereinafter called "the principal Regulations"), and the Public Health (Preservatives, &c., in Food) Amendment Regulations, 1926 (hereinafter called "the Regulations of 1926"), shall be construed together and may be cited together as the Public Health (Preservatives, etc., in Food) Regulations, 1925 to 1927.

2. The principal Regulations as amended by the Regulations of 1926 shall be further amended as follows:—

(1) The words "manufacture for sale or" shall be inserted after the words "prohibit the" in the first line of proviso (ii) to Article I.

(2) The following additional proviso shall be inserted at the end of Article 4 (1) and at the end of Article 11 (1)—

"(iii) The provisions of this Article shall not apply so as to prohibit the presence of sulphur dioxide in any article of food other than meat if it is shown either—

"(*a*) that the article not being an article specified in Part I of the said Schedule is intended to be used in the preparation of an article which is so specified, or

"(*b*) that the article being itself an article so specified, other than fruit or fruit pulp, is intended to be so treated before it is sold or exposed for sale by retail as to comply with the provisions of the Schedule as regards the proportion of sulphur dioxide contained."

(3) In Part 1 of the First Schedule for the item numbered 8 there shall be substituted the following items—

Food.	Preservative.	Parts per million.
8. Sugar (including solid glucose) and cane syrups.	Sulphur dioxide ..	70
8a. Cornflour (maize starch) and other prepared starches.	Sulphur dioxide ..	100

Given under the Official Seal of the Minister of Health this Eighth day of April, in the year One thousand nine hundred and twenty-seven.

(L.S.)

R. B. CROSS,
Assistant Secretary, Ministry of Health.

The Commissioners of Customs and Excise hereby consent to the foregoing Regulations so far as they apply to the Officers of Customs and Excise.

A. J. DYKE.
C. B. GRYLLS.

(a) 38–9 V. c. 55. (b) 54–5 V. c. 76. (c) 52–60 V. c. 20.
(d) 7 E. 7. c. 32. (e) 7 E. 7. c. 21.

* H.M. Stationery Office. Price 1*d.* net.

The following Circular has been sent to the Clerks of Authorities administering the Food and Drugs Acts :

CIRCULAR 782.*

PUBLIC HEALTH (PRESERVATIVES, &c., IN FOOD) AMENDMENT REGULATIONS, 1927.

SALE OF FOOD AND DRUGS ACT, 1927.

SIR,

1. I am directed by the Minister of Health to refer to Circulars 606 and 751, dated the 11th August, 1925, and the 16th December, 1926, respectively, and to forward for the information of the Authority a copy of the Public Health (Preservatives, &c., in Food) Amendment Regulations, 1927, which further amend the Public Health (Preservatives, &c., in Food) Regulations, 1925, in several matters of detail.

2. In view of the fact that the principal Regulations are already operative, it has been thought desirable that the amending Regulations should be issued as provisional Regulations, to come into operation forthwith, in pursuance of Section 2 of the Rules Publication Act, 1893. The provisional Regulations will continue in force until superseded by Regulations to the like effect, which it is proposed to make in accordance with the normal procedure under that Act. A copy of such Regulations will be sent to the Authority in due course.

3. The printing of the principal Regulations in the form in which they will operate as amended, to which reference was made in paragraph 5 of Circular 751, has been deferred pending the issue of the amending Regulations.

4. I am at the same time to draw the attention of the Authority to the Sale of Food and Drugs Act, 1927, which received Royal Assent on the 12th instant. The Act is designed to give effect to the recommendation of the Departmental Committee on Preservatives and Colouring Matters in Food that "any prohibitions or limitations imposed by the Regulations should bind the Courts in proceedings taken under the Sale of Food and Drugs Acts." Reference was made to this recommendation at the foot of page 1 of Circular 606. It will be noticed that the Act applies to all Regulations made under the Public Health (Regulations as to Food) Act, 1907, dealing with the composition of, or addition of any ingredient or material to, an article of food. Thus, the standards laid down by the Condensed Milk Regulations and the Dried Milk Regulations and the Dried Milk Regulations, as well as the prohibitions and restrictions in the Milk and Cream Regulations (which remain operative as regards cream until the 1st January, 1928), and in the Preservatives Regulations, will in future be conclusive for the purpose of proceedings under the Sale of Food and Drugs Act, 1875.

5. Copies of this Circular and of the provisional amending Regulations are being sent to the Medical Officer of Health and the Public Analyst.

R. B. CROSS,
Assistant Secretary.

* H.M. Stationery Office. Price 1*d* net.

Committee on Atomic Weights.

THIRTY-THIRD ANNUAL REPORT. DETERMINATIONS PUBLISHED DURING 1926.*

SMALL differences, attributed to differences in isotopic composition, are found by Briscoe, Robinson and Stephenson (*J. Chem. Soc.*, 1926, 70) in the densities of various specimens of boric oxide glass prepared from different mineralogical materials, but the oxides made from the first and last crystalline fractions of boric acid show identical densities (*ibid.*, 954). Baxter and Starkweather's density determinations give the atomic weight 14·006–14·008 for nitrogen (*Proc. Nat. Acad. Sci.*, 1926, **12**, 703) and the value 1·42897 for the density of oxygen (*ibid.*, 699). Robinson and Smith's values for the densities of silicon tetrachloride prepared from silicon of varying geological origin correspond with a difference of 0·005 in the atomic weight (*J. Chem. Soc.*, 1926, 1262). From measurements of the density of methyl chloride, Batuecas (*Anal. soc. españ. fís. quím.*, 1926, **24**, 528) obtains the value 35·465 for the atomic weight of chlorine. Continuation of the analysis of fractionated titanium tetrachloride by Baxter and Butler (*J. Amer. Chem. Soc.*, 1926, **48**, 3117) gives the value 47·903 for the atomic weight of titanium. By determining the silver yielded by the decomposition of silver oxide prepared by the interaction of silver nitrate and barium hydroxide in an atmosphere free from carbon dioxide, Riley and Baker obtained the average value 107·864 for the atomic weight of silver (*J. Chem. Soc.*, 1926, 2510). Preliminary measurements of the density of hydrogen iodide at different pressures by Moles and Miravelles (*Anal. soc. españ. fís. quím.*, 1926, **24**, 356) give 126·84 and 126·81 for the atomic weight of iodine. After allowing for the thorium present, Richards and Hall (*J. Amer. Chem. Soc.*, 1926, **48**, 704) find the value 206·02 for the atomic weight of radio-active lead extracted from very pure uraninite. Unsuccessful attempts to effect isotopic separation of ordinary lead and of a mixture of ordinary lead with uranium lead are recorded by Richards, King and Hall (*J. Amer. Chem. Soc.*, 1926, **48**, 1530). Aston finds with mercury the following isotopes in the proportions shown in brackets: 198 (4), 199(5), 200 (7), 201 (3), 202 (10) and 204 (2), which agree with the atomic weight 200·6 (*Nature*, 1926, **116**, 208), and with sulphur, approximately 3 per cent. of the isotopes S^{33} and S^{34} in the ratio 1:3 (*Nature*, 1926, **117**, 893).

For the atomic weights of hafnium, helium, holmium, lead, titanium, yttrium, and zirconium, the author suggests the respective values 178·6, 4·000, 163·5, 207·22, 47·90, 89·0, and 91·22, these being the only changes from the International Table for 1925.

T. H. P.

* G. P. Baxter. *J. Amer. Chem. Soc.*, 1927, **49**, 583–590.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Elimination of Sodium and Chlorine in Cow's Milk. L. Barthe and E. Dufilho. (*Ann. Falsif.*, 1927, **20**, 88–91).—One litre of milk from a healthy cow fed on a normal diet never contains more than 0·5 grm. of sodium or 1·5 of

chlorine, so that the ratio of sodium to chlorine is never greater than 0·339. These quantities were not exceeded even after the cows were given, on successive occasions, 25 and 50 grms. of marine salt. Addition of 1 grm. of sodium chloride per litre of milk increases the sodium in the milk by 0·393 and the chlorine by 0·606 grm., and 1 grm. of sodium carbonate increases the sodium by 0·2738. It is thus possible to detect adulteration by sodium chloride or any other salt of sodium. D. G. H.

Determination of Chlorine in Milk. A. D. Husband and W. Godden. (*Biochem. J.*, 1927, **21**, 259–261.)—The authors have investigated the suitability of the method of Austin and Van Slyke (*J. Biol. Chem.*, 1920, **41**, 345) and the method of Sisson and Dennis (*Amer. J. Dis. Child.*, 1921 **21**, 389) for the determination of chlorine in milk. Results were checked by means of Volhard titration after the milk was ashed with sodium carbonate or with lime. The modified picric acid solution, suggested by Sisson and Dennis, was used in each case. The results obtained are in entire agreement with the results of Austin and Van Slyke, but do not agree with the findings of Sisson and Dennis. The Sisson-Dennis method always gave results which were too high; and were liable to vary if changes were made in the ratio of milk to silver nitrate used in the determinations. A few tests were carried out on a chlorine-free solution of caseinogen and only by the method of Sisson and Dennis was any apparent chlorine content found. Therefore, to determine accurately the chlorine content of milk volumetrically by precipitation of the chlorine as silver chloride, it is essential that the protein be removed before the addition of the silver nitrate, as in the Austin and Van Slyke method. The technique used by the authors for the Austin and Van Slyke method is as follows:—To 20 c.c. of milk, measured into a small flask, were added 40 c.c. of 1·2 per cent. picric acid solution containing 2 c.c. of glacial acetic acid per litre, and, after 10 minutes, the curd was filtered off on a chlorine-free filter paper. Then 30 c.c. of clear filtrate were treated with 10 c.c. of 0·1 **N** silver nitrate solution, the mixture shaken and again filtered, and 20 c.c. of the clear filtrate were titrated against standard ammonium thiocyanate solution, as in the Volhard method. P. H. P.

Determination of Gelatin in Ice Cream. R. E. Remington and L. H. McRoberts. (*Ind. Eng. Chem.*, 1927, **19**, 267–269.)—Analysis of 28 samples of commercial gelatin, such as is used in ice cream, showed that the average nitrogen content was 14·84 per cent., and the specific rotation −117°, corresponding with 17·53 per cent. and −139°, respectively, on the dry, ash-free substance. To determine gelatin in ice cream, 200 grms. of the melted and well mixed sample are diluted with 25 c.c. of water, haematoxylin indicator is added, the mixture heated at 40° C., and 10 per cent. acetic acid is added until the pink colour of the indicator has disappeared completely. Water is then added to make the weight up to 250 grms., the mixture is heated at 40° C. until the curd has separated, and filtered through linen. One hundred grms. of the filtrate are treated with 3 c.c. of saturated potassium alum solution and 200 c.c. of 95 per cent. alcohol, cooled,

the precipitate collected on a filter paper, the filter and precipitate then placed in a small quantity of water, and, when the gelatin has had time to swell, the volume of the water is increased to 50 c.c., and the mixture is boiled and filtered. The filtrate is cooled and diluted to 100 c.c. The rotation of this solution is then determined at 35° C. The weight of serum to be used as a basis in the calculation is obtained by subtracting the weight of fat and casein in 200 grms. of the sample from 250 grms. The percentage of gelatin in the sample is $0{\cdot}00074 \times R \times W$, R being the reading in a 200 mm. tube and W the weight of serum. The nitrogen is also determined in 25 c.c. of the solution. If N is mgrms. of nitrogen in the 25 c.c. of solution and W the weight of serum, the percentage of gelatin in the sample is $0{\cdot}135 \times N \times W$. W. P. S.

Chemical and Physico-Chemical Changes accompanying the Beginning of the Putrefaction of Flesh. J. Tillmans, P. Hirsch and A. Kuhn. (*Z. Unters. Nahr. Genussm.*, 1927, **53**, 44–64.)—Extracts of fish and of cooked and uncooked meat (principally beef) taken from various parts of the animal were prepared by digestion of the sample with water, and their physical and chemical properties determined daily as putrefaction proceeded. The refractive index, reduction-potential, surface-tension, titration in stages to various P_H values, and conductivity in the presence of acid or alkali showed no progressive alteration with the time. The order of the values of the conductivity may be correlated with the amounts of electrolytes (chiefly sodium chloride) present in the sample, as indicated by the lowering of the freezing point. The colour produced with Nessler's reagent after 6 minutes, and matched with potassium dichromate solution, increased progressively with the putrefaction in meat, but not in fish. No substantial differences in the amountsof glycogen, purine bases and creatinine were detected between the first and later stages of putrefaction, but the iso-nitrile reaction for primary amines was found to be a good indication of glycogen. The titration of the volatile acids and bases, separated by steam-distillation of the sample with acid and alkali, respectively, and the determination of their molecular weights, may be used as a guide to the progress of putrefaction in particular cases. Catalytic enzymes were found in all the samples investigated, to various extents, and the beginning of putrefaction was accompanied by a great increase in their activity. Negative results, however, were obtained in tests for diastase and proteolytic enzymes. J. G.

Determination of Cuprous Oxide produced in Sugar Analysis. C. S. Bisson and J. G. Sewell. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 120–124.)—The usual method for the determination of reducing sugars by means of Fehling's solution may be shortened by the complete oxidation of the freshly precipitated cuprous oxide (filtered and washed on an asbestos filter), by a known excess of standard potassium permanganate solution. A solution of 18 N sulphuric acid is then added, and, as soon as all the particles have dissolved, a freshly standardised solution of ferrous sulphate is run in from a burette till an excess (5 to 10 c.c. above the amount required to decolorise the solution) is present. This excess

is then back-titrated with the potassium permanganate solution. Results in close agreement with the gravimetric and electrolytic methods have been obtained for sugar from plant products and for pure dextrose. J. G.

Rapid Method for the Determination of Starch. O. S. Rask. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 108–120.)—Starches dispersed in hydrochloric acid solutions containing 21 grms. of hydrogen chloride in 100 c.c. of water, at 25°C., or a lower temperature, for a period of less than 45 minutes, may be coagulated quantitatively by means of alcohol, filtered on a Gooch crucible, dried at 105°C., and weighed. In the case of wheat flour it is advisable first to destroy any gluten-forming properties by three extractions with alcohol (70 per cent. by volume). This acid treatment is carried out by the gradual addition of the acid to the ground sample till solution is effected on stirring. The starch must then be coagulated by 96 per cent. alcohol within 35 minutes, in order to avoid hydrolysis. The method is specific for starch. Negligible quantities of adsorbed or occluded substances were detected in the coagulum, which was free from celluloses, hemi-celluloses, proteins, fat and mineral matter. If large quantities of polysaccharides are present, however, (*e.g.* dextrins and pectins from linseed meal) these may not be removed by the alcoholic wash-liquor. Satisfactory results have been obtained for wheat, potato, and corn starches, and for patent flour and oatmeal. The results are higher than those given by the official (A.O.A.C.) diastase method, but probably represent more closely the true figures. J. G.

Chemical Composition of Tunisian Olive Oil. G. S. Jamieson, R. M. Hann and W. F. Baughman. (*Oil and Fat Ind.*, 1927, **4**, 63–65.)—Oil expressed from olives grown in the Sousse district of Tunis had the following characteristics :— Sp. gr. at 25°, 0·9131 ; n_D^{20}, 1·4700 ; acid value, 1·9 iodine value (Hanus) 86·0 ; saponification value, 193·6 ; unsaponifiable matter (iodine value 117·0), 0·8 per cent. ; acetyl value, 8·3 ; saturated acids (iodine value 6·1), 16·5 per cent.; unsaturated acids (iodine value 103·8), 77·6 per cent. The unsaturated acid fraction was calculated to contain oleic acid 85·21 and linolic acid, 14·79 ; and the saturated acids to contain myristic, 0·82 ; palmitic, 83·44 ; stearic, 14·19 ; and arachidic acid 1·55 per cent. The above figures show that Tunisian olive oil closely resembles Californian and Italian oils, except that it contains a considerably higher percentage of saturated acids and a lower percentage of unsaturated acids (14–15 per cent. less of oleic acid glyceride and about three times as much linolic glyceride).

D. G. H.

Errors in Analysis of Alkaloids caused by the Presence of Fatty Acid or Soap. H. R. Watkins and S. Palkin. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 130–135.)—In the determination of alkaloids in compressed tablets by extraction with chloroform from an aqueous solution and subsequent titration, high results may be obtained from fatty acids, present originally as calcium or magnesium soaps, which are extracted with the alkaloid. Fatty acids present in the form

of ammonium or sodium soaps do not affect the titration, although they also may be carried over as a result of hydrolysis of the soap. Complete details are given of a method in which the fatty acids are removed from the acid solution containing the alkaloid (atropine). A method is also described which avoids the formation of unmanageable emulsions during the extraction process. J. G.

Stomatal Numbers—Their Value for distinguishing Plant Species. H. A. Timmerman. (*Pharm. J.*, 1927, **118**, 241–243.)—To determine the value of stomatal figures for differentiating between closely related species, an examination of the number per sq. mm. of leaf surface for *Datura stramonium*, *D. Tatula*, *D. laevis* and *D. innoxia* was made, and showed that for the upper and lower leaf surfaces variations from the mean were from 16 to 29 and 6 to 29 per cent., respectively, whilst the ratio of stomata on the two surfaces was more constant, varying from 4 to 12 per cent. from the mean. The number of palisade cells per sq. mm. of leaf surface also varied widely, and the same conditions that caused variation in the number of stomata also affected the palisade cells, but such variations were not found to be proportional. It is important to state the range of variation when giving stomatal figures, as well as the most commonly occurring figure. *D. innoxia* was the only one of the four species examined that could be distinguished by the number of stomata, and this was because the number of stomata on the two leaf surfaces are, for this species, practically the same. D. G. H.

Biochemical, etc.

Gasometric Determination of Small Amounts of Carbon Monoxide in Blood, and its Application to Blood Volume Studies. D. D. Van Slyke and F. S. Robscheit-Robbins. (*J. Biol. Chem.*, 1927, **72**, 39-50.)—A technique is described for the quantitative gasometric determination of small amounts of carbon monoxide in blood. It was developed primarily to make possible the determination of blood volumes by the carbon monoxide method of Grehant and Quinquaud (*Compt. rend.*, 1882, **94**, 1450) without saturating as much as one-third of the blood haemoglobin with carbon monoxide in order to obtain accurate results. It is shown that 4 minutes after the injection of carbon monoxide blood (blood saturated with the gas), as described in the paper, one can determine the volume of the circulating red cells from the blood carbon monoxide content with less than 5 per cent. error due to analytical technique and carbon monoxide distribution within the blood. The magnitude of the possible additional error due to diffusion of carbon monoxide from blood to tissue haemoglobin has not been ascertained. The results of two experiments on dogs are given. P. H. P.

Micro-Determination of Iron in Blood. F. H. Smirk. (*Biochem. J.*, 1927, **21**, 36–39.)—With the use of the recent method of Fowweather (*Biochem. J.*, 1926, **20**, 93) for the determination of iron in blood, occasional bumping and loss of samples was found troublesome. A shorter method for a series of determinations has now been elaborated, entirely without risk of bumping and with

probably a greater accuracy than that claimed by Fowweather. The method depends on the rapid oxidation of blood proteins by ammonium persulphate and nitric acid, with subsequent colorimetric determination of iron as ferric thiocyanate in the presence of acetone, against an artificial colour standard. For each sample 0·2 c.c. of blood is required. Full experimental details and practical precautions are given. The artificial standard consists of:—4 c.c. of cochineal solution (B.D.H. Indicator), 3·2 c.c. of methyl red solution (B.D.H. Indicator) and 4 c.c. of dilute hydrochloric acid (1 in 5) mixed and diluted with equal parts of acetone and water to the approximate depth of colour of a standard iron solution. A final adjustment of tint is made by the addition of drops of methyl red if the orange tint predominates, and of cochineal solution if the red is too pronounced. The colour is permanent and indistinguishable from that of the thiocyanate. Equivalent amounts of the ammonium persulphate and nitric acid in each sample are added to the iron standard; since they contain traces of iron. Some of the results obtained are given. P. H. P.

Colorimetric Determination of Cystine and Glutathione. G. Hunter and B. A. Eagles. (*J. Biol. Chem.*, 1927, **72**, 177–183.)—A colorimetric method, based on the method of Folin and Looney (*J. Biol. Chem.*, 1922, **51**, 427) is described for the accurate determination of cystine and glutathione in simple solutions. The method of Folin and Looney is criticised; the chief difficulty encountered with it lay in the use of sodium carbonate as alkali, and this was overcome by the use of sodium hydroxide instead. It is shown that 4·64 parts of pure cystine yield the same amount of colour as 10 parts of the purest glutathione prepared by the authors. Cystine, which is easily obtained pure, is a desirable standard for the comparison of glutathione prepared by different workers, since there is a doubt as to the purity of the latter substance. The amount of cystine in hydrolysed glutathione has also been measured. The method is not yet applicable to the determination of glutathione in tissue extracts, since certain other substances present give a blue colour with the reagents. Three of these are cysteine, uric acid and sympectothione. Cysteine and sympectothione will interfere with the iodine method of Tunnicliffe (*Biochem. J.*, 1925, **19**, 194) for the determination of reduced glutathione. By the method described cystine should be measurable in protein hydrolysates, if the assumption of Folin and Looney is correct, that no other substances in protein hydrolysates yield a colour by their method. P. H. P.

Effect of Heat and Oxidation on the Nutritive Value of a Protein. H. Goldblatt and A. R. Moritz. (*J. Biol. Chem.*, 1927, **72**, 321–326.)—An investigation was carried out to determine whether the inactivation of casein at the extremes of temperature used by previous investigators makes any appreciable difference in its nutritive value, and thus introduces a source of error in experiments which deal with the testing of diets for growth-promoting properties. There was no significant difference as regards growth between two groups of rats which received similar complete diets containing 20 per cent. of casein oxidised

for 36 hours at 110 and 130°C., respectively. Both groups grew normally, and thus the inactivation of casein by oxidation at 110 and 130°C. for 36 hours did not change the nutritive value of this protein. The various temperatures between 110 and 130°C. at which casein has been heated and oxidised for the inactivation of vitamins *A* and *D* in casein cannot have been a source of error in the results heretofore published, when the proportion of casein in those diets was well above the minimum. P. H. P.

Growth Experiments on Diets Rich in Fat. H. Levine and A. H. Smith. (*J. Biol. Chem.*, 1927, **72**, 223–238.)—Experiments show that growth at a normal rate from 30 to 180 grms. in body weight can be induced in rats on a high fat ration practically devoid of preformed carbohydrate and containing 86 per cent. of the total calories in the form of fat, provided the protein and salt requirements of the animal are fulfilled. The livers of some rats that had been on the above high fat ration for a period of 83 days, when examined microscopically, did not contain fat droplets, although Chalatow (*Virchows Arch. path. Anat.*, 1912, **207**, 452) fed rats on egg yolk and milk, and the livers of these rats showed fat droplets until after 4 months on the ration. Comparisons were made of the efficiency *in growth*, of calories furnished, on the one hand, by the high fat diet, and, on the other hand, by a better balanced ration (containing 39 per cent. of calories derived from carbohydrate and 47 per cent. of the calories in the form of fat). Rats receiving a maximum of calories in the diet in the form of fat can grow as efficiently, measured by energy cost, as when the ration contains a mixture of fat and carbohydrates. Determination of fat utilisation on the high fat diets here used showed that the rat can utilise from 98 to 99 per cent. of the ingested fat. P. H. P.

Relation of Cholesterol to Vitamin *D*. O. Rosenheim and T. A. Webster. (*Biochem. J.*, 1927, **21**, 127–129.)—Since no derivatives of sterols which were either active by themselves or could be rendered antirachitic by irradiation have been found, the problem has been re-considered. A brief summary of previous results is given. The question of how far the purity of the cholesterol employed is related to its capacity for activation by ultra-violet light has been investigated. A repeatedly recrystallised specimen of cholesterol (m. pt., 148–9°C.) was converted into the dibromide, which was then reduced to cholesterol by means of sodium amalgam in the presence of acetic acid. The purified substance had the same m.pt. and gave the usual colour reactions. Irradiation and biological tests showed that purification by way of the dibromide completely deprived this cholesterol, which would previously have been considered as "chemically pure," of its power to become antirachitic by irradiation with ultra-violet light. Thus the precursor of vitamin *D* is not cholesterol itself, but a substance which is associated with and follows "chemically pure" cholesterol in all its stages of purification by the usual methods (esterification, saponification, recrystallisation). The provitamin may be a substance allied to cholesterol in character

Ordinary " pure " cholesterol yields 0·1 per cent. of active substance. The cholesterol prepared by the dibromide method did not give the ordinary " pure " cholesterol absorption spectrum. *Addendum.*—It has since been found by the authors that ergosterol, or a sterol of similar constitution, is the parent substance of vitamin *D*. (*Cf. Lancet*, February 4, 1927). P. H. P.

Bacteriological.

Standards for Milk Pasteurisation. C. E. North and W. H. Park. (*Amer. J. Hyg.*, 1927, 7, 147–173.)—Irregularities in the recorded thermal death point of the tubercle bacillus are to be attributed mainly to faults in the heating equipment and its operation by the investigators. There is no material difference in the resistance to heat between bovine and human strains of tubercle bacilli, or between different strains of either species, or between the tubercle bacilli in naturally infected milk, tissue lesions, or pure cultures. Some of the work done by previous investigators furnished reliable results. These indicate several thermal death points, as follows : 212° F. to 185° F., when heated for a few seconds ; 180° F. for 2 minutes ; 170° F., for 5 minutes ; 140° F., for 20 minutes. The care with which the work recorded in *Bull. No.* 147 (U.S.A. Public Service, 1925), was done, and the standing of the investigators, justify the conclusions therein, *viz.*, that tubercle bacilli are killed at 138° F. when heated for 30 minutes, and that a standard of 142° F. for 30 minutes is a proper one for pasteurisation. For each period of time there is a degree of temperature at which tubercle bacilli are destroyed, and this relationship may be properly described as a " thermal death curve " rather than a " thermal death point." The principal series of times and temperatures determined by the authors were as follows :—At 212° F., 10 seconds ; 200° F., 20 seconds ; 180° F., 20 seconds ; 170° F., 20 seconds ; 160° F., 20 seconds ; 155° F., 30 seconds ; 150° F., 2 minutes ; 145° F., 6 minutes, 142° F., 10 minutes ; 140° F., 10 minutes ; 138° F., 20 minutes ; 136° F., 30 minutes ; 136° F., 40 minutes ; 132° F., 60 minutes ; 130° F., 60 minutes. Temperature standards for pasteurisation which injure the milk are not necessary for the protection of public health. The standard of 145° F., advocated by some authorities, changes the appearance of milk and thereby discredits pasteurisation in the minds of milk consumers. It is in the interest of public health that pasteurisation should be everywhere accepted. Its acceptance is prevented by such milk injuries. Standards used by New York City and fifteen other large cities for more than ten years have been proved by the experience of the health authorities of these cities satisfactory safeguards over public health, and at the same time have not injured the milk in a way that would prevent its acceptance by the public. These standards are a minimum temperature of 142° F. for a minimum time of 30 minutes. The results of the researches of previous investigators and of the authors' investigations show that this pasteurising standard provides an adequate margin of safety.

The paper concludes with a bibliography containing 26 references.

Germicidal values of Australian Essential Oils and their pure Constituents. (*Perf. and Ess. Oil Rec.*, 1927, **18**, 100–101.)—The determination of Rideal–Walker coefficients of essential oil constituents and synthetics is continued for a series of aliphatic aldehydes and ketones of the C_8–C_{12} series. They are characterised by high coefficients, and the dispersion of the various substances examined varied according to the medium used. When substances are dispersed in ethyl alcohol the germicidal effect of the medium must be taken into account with low coefficients, but with values over 4 may be neglected. Alcohols, as a rule, were more evenly dispersed than aldehydes. The sesquiterpenes, in general were found to possess comparatively poor germicidal properties. Rideal–Walker coefficients for the following crude oils were :—*Fusanus spicatus* (West Australian sandalwood oil) 1·5 ; (chief active constitutents, sesquiterpene alcohols) ; *Santalum album* (East Indian sandalwood oil), 1·5 (Sesquiterpene alcohols) ; *Zieria macrophylla* 2·2 (chief active constituent, zierone). D. G. H.

Sugar-Tolerant Yeasts in Chocolate-coated Creams. M. B. Church, H. S. Paine, J. Hamilton. (*Ind. Eng. Chem.*, 1927, **19**, 353.)

Prevention of " Bursting " in Chocolate-coated Fondant Creams. H. S. Paine, V. Birchner, and J. Hamilton. (*Ibid.*, 358.)—The cause of " bursting " in chocolate creams has been traced to the presence of yeasts, in many cases torulae, producing minute quantities of gas in the presence of sugar syrups of high concentration. The growth of these yeasts and fermentation by them can be prevented by (*a*) maintaining proper sanitary conditions in the factory ; (*b*) sterilising the ingredients (sugar and fruit-pieces) ; and (*c*) increasing the concentration of the sugar in solution in the cream above 79 per cent., by the use of glucose and invert sugar or by the addition of invertase before moulding the cream centres. R. F. I.

Micro-Mounting of Mould Fungi. (*Microsc. Rec.*, 1927, **10**, 28 ; *Pharm. J.*, 1927, **118**, 308.)—The best medium for mounting such moulds as *Aspergillus* and *Penicillium*, which become tangled masses in water, is lactophenol, made up of phenol 2 parts, lactic acid (sp. gr. 1·5), 2 parts, glycerin 1, and distilled water 2 parts. A ring of cement round the cover glass then gives permanent mounts. The use of a saturated solution of picric acid instead of water causes the mould to take most of the stain, leaving a nearly colourless background. D. G. H.

Carbon Monoxide Poisoning of Bacteria in the Absence of Haemoglobin. P. F. Frankland. (*Nature*, 1927, **119**, 491–492.)—Experiments were carried out in 1886 (*Proc. Royal Soc.*, **45**, 292–301) on the exposure of *Bacillus pyocyaneus*, Koch's spirillum of Asiatic cholera and Finkler's spirillum, in the form of gelatin-peptone plate cultures exposed to atmospheres of carbon monoxide, nitric oxide, hydrogen sulphide, sulphur dioxide and nitrous oxide respectively, with controls in air. In the case of carbon monoxide the poisoning effect of the gas was not permanent, the number of colonies developing from 1 c.c. of culture

being for *Bacillus pyocyaneus*, air plates (4 days) 113,978, carbon monoxide plates (7 days) 0, rising to 100,821 on subsequent transference to air ; for Koch's spirillum, 52,020 and 19,494 with no increase in air ; and for Finkler's spirillum (3 days in air) 4574 and 2 increasing to 501 in air. Nitric oxide, hydrogen sulphide and sulphur dioxide rapidly and permanently poisoned the colonies, whilst in nitrous oxide the development of colonies was in all cases far below the air control plates, but after transference to air more colonies developed, the effect being very similar to that of carbon monoxide. It is suggested that " strains " of organisms might be bred endowed with capacity to resist the inhibiting effect of a particular gas, and that behaviour towards a toxic gas might be of use in bacteriological diagnosis. D. G. H.

Toxicological and Forensic.

Carbon Monoxide Poisoning in Forensic Cases. D. J. A. Kerr. (*Brit. Med. J.*, 1927, March 5, 415-418.)—The increasing medico-legal importance of carbon monoxide poisoning is shown by the Registrar General's statistics for suicidal deaths in Scotland. In 1913 the figures for suicide by coal gas were 10, and in 1924, 88. In England a similar increase is found, the number of suicides by means of coal gas having risen from 213 in 1919 to 762 in 1925—a striking contrast to the number of accidental deaths, which has remained almost constant (149 in 1918, 133 in 1924, and 163 in 1925). One of the most important questions in such cases of poisoning is whether death was the result of accident, suicide or murder.

The difficulties involved are illustrated by a case that occurred this year. A labourer employed in working down a well was found dead in bed. *Post-mortem* examination showed that death was due to carbon monoxide poisoning, and the man's wife stated that he had complained of a smell of gas in the well, and that his clothes smelt strongly of gas when he returned from work. Enquiry showed that he had returned from work at mid-day on Saturday, and was seen walking about the town in the afternoon and evening. He had returned home about midnight, and had apparently cooked himself some supper in the kitchen, which contained a coal fire and also a gas ring. Next morning he was found dead in bed in the kitchen, but his wife stated that she noticed no smell of gas nor did she find the tap turned on.

The question to be determined was whether this was a case of accidental death from exposure to coal gas at his work, or whether it was suicide or a case of homicide ; or whether it was a case not of coal gas poisoning, but of *post-mortem* development of nitroxy-haemoglobin to which Haldane has drawn attention (ANAL ST, 1925, **50**, 520). A determination of the percentage saturation of the blood by means of Hartridge's reversion spectroscope (ANALYST, 1923, **48**, 341) excluded the last-named possibility. The saturation was over 70 per cent., and the man could therefore not have walked about for 12 hours without showing the usual symptoms of carbon monoxide poisoning. Apart from this fact, a much

lower saturation than 70 per cent. causes unconsciousness, and carbon monoxide is rapidly eliminated from the blood when the patient breathes fresh air, so that after five or six hours only an infinitesimal amount is present. There could thus be no doubt that the man became unconscious in the atmosphere which contained the carbon dioxide, and that he was gassed in the dwelling house.

This case illustrates most of the questions arising in cases of carbon monoxide poisoning,—namely (1) the possibility of mistaken diagnosis; (2) the toxicity and amount of saturation required to produce unconsciousness; (3) the time elapsing before a person becomes unconscious; (4) the rate of elimination. With regard to the first of these questions Haldane (*loc. cit.*) reported a case in 1925, where the verdict at the inquest was given as " carbon monoxide poisoning contracted during employment." On investigation it was proved that the *post-mortem* appearances attributed to carbon monoxide poisoning were really due to nitroxy-haemoglobin, which gives similar reactions in the usual tests, such as a pink colour on dilution, Kunkel's tannic acid test, and the spectroscopic test. Carbon monoxide poisoning can, however, be distinguished from nitroxyhaemoglobin by boiling a dilute solution of the blood, or by means of Hartridge's reversion spectroscope (*loc. cit.*). The *post-mortem* condition of nitroxyhaemoglobin is rare, and the circumstances are usually sufficient to exclude it, although in the case referred to above, its possibility had to be taken into consideration.

The symptoms caused by a given percentage saturation of the blood with carbon monoxide vary with the individual and the rapidity with which saturation has taken place. Distinct symptoms of malaise and weakness are present with a saturation of 50 per cent.; between 50 and 55 per cent. any exertion, such as walking, is difficult, and above this unconsciousness is produced. When the accumulation in the blood is rapid, the degree of saturation required to produce the above symptoms will be less. The rapidity with which carbon monoxide accumulates in the blood varies with the amount of the gas present in the air. An individual breathing an atmosphere containing 1 per cent. of carbon monoxide will have 50 per cent. of carbon monoxide in his blood in fifteen or sixteen minutes. Exposure for twenty minutes is thus approximately the time required for unconsciousness to develop with this percentage in the air. If a person puts his head in a gas oven he will be breathing almost pure coal gas, which in Edinburgh contains at present 22 per cent. of carbon monoxide. Under such conditions unconsciousness will theoretically occur in about thirty seconds. The rate of elimination of the gas after the patient has been removed from the atmosphere of carbon monoxide is also of importance from the medico-legal standpoint. Henderson (*Brit. Med. J.*, 1926, Jan. 9, p. 41) has shown that for the first hour and a half the elimination is small, but after that becomes rapid, and, provided the patient lives, all the carbon monoxide should have been eliminated in from five to six hours.

In the case quoted by Haldane, to which reference has been made, the verdict of carbon monoxide poisoning at the inquest was founded on the bright pink colour of the blood seen at the *post-mortem* examination, and on the positive results

obtained from the usual tests for carbon monoxide. Fourteen days, however, had elapsed before death occurred, so that in this case it is evident that the appearances and positive tests could not have been due to carbon monoxide gas. Had the above facts connected with gas poisoning been more widely known, this mistake could not have occurred.

The Action of Blood on Sulphides. W. Denis and L. Reed. (*J. Biol. Chem.*, 1927, **72**, 385–394.)—In view of the constant occurrence in the intestine, the high coefficient of absorption, and intensely toxic properties of hydrogen sulphide, it is clear that, as under ordinary conditions no objectionable symptoms are noted, there must exist in the body some efficient mechanism for the detoxication of this substance. An attempt has been made to obtain evidence regarding the nature of the oxidation products of hydrogen sulphide formed when this substance is introduced into the blood stream or placed in the intestine of the living animal. Samples of blood withdrawn at intervals after the administration of sulphides have been analysed for inorganic and ethereal sulphates and neutral sulphur by the gravimetric methods of Denis and Reed (*J. Biol. Chem.*, 1926, **71**, 191). Analysis of the blood of dogs which had received sodium sulphide by intravenous injection, or by injection into the intestine, sometimes showed a rise in the inorganic sulphate, but no increase in the neutral sulphur fraction. These increased values were noted particularly in the case of animals in which the kidneys had been tied off. The results are believed to give support to the theory that hydrogen sulphide is detoxicated by oxidation to sulphuric acid. P. H. P.

Agricultural Analysis, etc.

Detection and Determination of Nitrogen-Bearing Chemicals added to Animal or Vegetable Nitrogenous Manures. H. C. Moore and R. White. (*Ind. Eng. Chem.*, 1927, **19**, 264–266.)—The presence of such substances as ammonium sulphate, cyanamide, urea, etc., in so-called nitrogenous tankage may be detected by mixing a portion of the sample with carbon tetrachloride; cyanamide and ammonium sulphate settle to the bottom and may be identified by the usual tests. If the upper portion, consisting of tankage and carbon tetrachloride, is then mixed with an equal volume of turpentine, crystals of urea (when this is present) will appear floating or in partial suspension. The following methods are recommended for the determination of these substances. *Cyanamide and nitrate nitrogen.*—Five grms. of the sample are shaken for one hour with 250 c.c. of water, and the solution is filtered; nitrate nitrogen is determined in 50 c.c. of this solution by reducing it with reduced iron in slightly acid solution and distilling the resulting ammonia; allowance is made for any ammonia present as such, and a separate portion of 50 c.c. of the solution is used for this determination. *Cyanamide.*—Fifty c.c. of the solution are treated with an excess of 1 per cent. silver nitrate solution and 20 c.c. of 10 per cent. potassium hydroxide solution, the brown precipitate is collected, washed, and the nitrogen in it determined by Kjeldahl's method. *Urea.*—Five grms. of the sample are shaken for thirty

minutes with 100 c.c. of alcohol, the mixture is filtered, the insoluble portion washed with alcohol, and the filtrate and washings are diluted with alcohol to 250 c.c. ; 50 c.c. of the alcoholic solution are mixed with 50 c.c. of water, evaporated to 40 c.c. to remove alcohol, then diluted with 100 c.c. of water, and treated with 0·25 grm. of urease. After thirty minutes the resulting ammonia is distilled and titrated. The portion of the sample insoluble in alcohol is shaken with water, diluted to 250 c.c., and filtered ; 50 c.c. of the filtrate are distilled with magnesium oxide to determine the quantity of ammoniacal nitrogen present. If urea is not present, the ammoniacal nitrogen may be determined as described above, but extraction with alcohol will remove small amounts of urea usually present in organic materials. W. P. S.

Organic Analysis.

Reactions of Lead Tetra-Ethyl. O. H. Browne and E. E. Reid. (*J. Amer. Chem. Soc.*, 1927, **49**, 830–838.)—Improved methods of preparing triethyl-lead chloride, hydroxide and acetate are given. The first is best obtained by the action of concentrated hydrochloric acid on lead tetra-ethyl at 30–33° C. The acetate and salts of other organic acids are preferably prepared directly from lead tetra-ethyl and the acids with the help of silica gel as a catalyst ; a number of such compounds are described. The triethyl lead salts of the halogenated fatty acids are difficult to handle owing to their pronounced sternutatory properties.

On addition of silica gel, lead tetra-ethyl reacts readily with acetyl chloride at room temperature, gradually depositing prisms of triethyl-lead chloride. Benzoyl chloride also reacts, but the only products that could be isolated were lead chloride and benzoic acid. In carbon disulphide, lead tetra-ethyl and phosphorus pentachloride give a syrupy liquid containing triethyl-lead chloride. When aluminium chloride is dropped on to lead tetra-ethyl, a violent reaction occurs, with formation of a cloud of finely divided lead ; dilution with a solvent moderates this reaction, triethyl-lead chloride and a gas being then formed. Silicon tetrachloride reacts with lead tetra-ethyl to give triethyl-lead chloride, and titanium tetrachloride is reduced, giving a brown tarry substance which is coloured purple by the titanium trichloride. T. H. P.

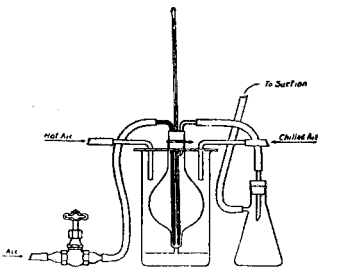
New Reaction for Eugenol. C. J. Enklaar. (*Chem. Weekblad*, 1927, **24**, 115–116.)—Eugenol in essential oils may be detected by a solution of manganic sulphate in water containing acetic acid. A precipitate is produced which has the appearance of a red oil, is soluble in benzene, and, if heated with water, produces a yellow solid containing manganese and carbon. Fusion with potassium hydroxide and nitrate produces a green mass, which turns brown on the addition of water. The reagent, which must be freshly prepared, is made by the action of powdered manganese sulphate and potassium permanganate on a hot solution of acetic acid. Citral, linalol and myrcene do not give the reaction. J. G.

Simple and Rapid Reaction to distinguish Aniseed Oil from Star Anise Oil. W. P. H. van Den Driessen Mareeuw. (*Pharm. Weekblad*, 1927, **64**, 189–195.)—Star anise oil (10 c.c.) is shaken in a flask with 1·25 grms. of potassium ferricyanide dissolved in 4 c.c. of water, and 12·5 c.c. of a 20 per cent. solution of hydrochloric acid. The heavy, bulky precipitate is filtered, and dried between filter papers till all traces of oil have been removed. A small quantity of needle-shaped crystals remains, which have the composition $C_{10}H_{18}O,H_3Fe(CN)_6,3H_2O$. Under similar conditions aniseed oil yields an opalescent oil, not a bulky precipitate or crystals. Potassium ferrocyanide produces analogous effects, and both reagents also behave characteristically with eucalyptus oil. J. G.

An Odoriferous Oil and two New Linolic Tetrabromides from Philippine Lumbang Oil. S. Santiago and A. P. West. (*Phil. J. Sci.*, 1927, **32**, 41–52.)—In addition to the mixture of unsaturated glycerides (linolenic, linolic and oleic) which are its chief constituents, lumbang oil contains an intensely odoriferous oil which comes over on steam distillation, and which boils at 80–84° C., is soluble in water and various organic solvents, and gives positive tests for aldehydes and unsaturated compounds. Four linolic tetrabromides were isolated which may have been derived from the four isomeric linolic acids. The m.pts. of these were, α, 112·3–114·3° C.; β, 59–60° C.; γ, liquid; δ, 57–58° C.; bromine content (in same order) 53·73; 53·44; 53·47 and 53·28; solubility in 100 c.c. of cold methyl alcohol at 27° C., β, 0·7463; δ, 0·2164; crystal form, β, rods in bundles; δ, needles in bundles. On concentrating the alcohol filtrate from the α tetrabromide a red oil separated which gradually deposited silky crystals consisting of a mixture of the β and δ compounds, which could then be separated by means of methyl alcohol; these do not appear to have been previously described. D. G. H.

Determination of the Asphalt Content of Mineral Oils. J. Marcusson. (*Chem. Zeit.*, 1927, **51**, 190.)—The various methods proposed for determining the asphalt in mineral oils yield widely divergent results, since some of them determine other constituents in addition to the asphaltenes, which are usually assumed to be the only harmful components. The following method determines only the asphaltenes, which are found to be precipitable in the form of double compounds with ferric chloride. Five grms. of the oil are dissolved in 50 c.c. of ether, and the liquid treated with 5 c.c. of a 5 per cent. ethereal ferric chloride solution and left for 2 hours. The precipitate is then transferred to a pleated filter and washed once with ether. When the filter becomes dry, it is tied up with a thread and boiled with successive quantities of ether as long as oil or paraffin wax is extracted. It is next heated in the same flask with chloroform, which dissolves the double compound. The dark solution thus obtained is shaken in a small separating funnel, first with 5 c.c. of dilute hydrochloric acid to decompose the double compound, and then with 5 c.c. of water, and the residual asphalt dried for a short time at 105° C., and weighed. T. H. P.

Determination of Paraffin Wax in Crude Wax. L. M. Henderson and S. W. Ferris. (*Ind. Eng. Chem.*, 1927, **19**, 262–264.)—Nitrobenzene is used as the solvent for separating the oil from the wax, and the apparatus employed is shown in the diagram. The flask has a short length of glass rod sealed to the lower narrow part, and this rod fits into a hole in a layer of asbestos cement at the bottom of the beaker. Ten grms. of the sample and 20 c.c. of nitrobenzene are placed in the flask and the cork is inserted, but the short tube is not at this stage connected with the suction pump. Hot air is passed into the beaker until the mixture is heated to 70° C., and air is bubbled slowly through the mixture. As soon as the temperature reaches 70° C., the supply of hot air is cut off and cold air is admitted to the beaker, the current of air through the mixture being accelerated slightly during the cooling. The mixture is kept at 32° C. for five minutes, the cork is removed, and the nitrobenzene solution at the bottom of the flask is withdrawn by means of a capillary tube. Another portion of 20 c.c. of nitrobenzene is then added, and the process repeated. After the second separation, the residue of wax in the flask is heated at 135° C., and the short tube is connected with the suction pump; the residual nitrobenzene is thus removed rapidly. The temperature is then increased to 150° C., and air is bubbled through the wax for fifteen minutes. The melting point of the wax may now be determined in the flask by introducing a thermometer and noting the temperature every thirty seconds. When quite cold, any wax adhering to the thermometer is scraped off and returned to the flask, and the yield of wax is determined by weighing. Nitrobenzene is preferable to acetone as a solvent for the oils, one advantage being that its complete removal from the wax can be ascertained by the disappearance of its characteristic odour. W. P. S.



Evaluation of Turbine Oils. T. H. Rogers and C. E. Miller. (*Ind. Eng. Chem.*, 1927, **19**, 308–312.)—The deterioration which turbine oils undergo in service is due to oxidation, with the formation of asphaltic substances insoluble in the oil and of free acids which are soluble in the oil. In the presence of water these acids form soaps when in contact with metals such as iron or copper. A stability test is described in which the oil is heated at 100° C., and oxygen, passed previously through water, is conducted through the oil at the rate of two or three bubbles per second. Samples of the oil are withdrawn every forty-eight hours and tested for acidity and demulsibility. The test may also be made in the presence of iron (a length of 18-gauge wire). Results of comparative test runs show that this stability test substantially duplicates the behaviour of oils in a dry turbine. W. P. S.

New Method of Separating *p*-Cresol from its Isomerides and a Study of its Boiling Point. H. D. Gibbs. (*J. Amer. Chem. Soc.*, 1927, **49**, 839–844.)—*p*-Cresol may be freed from its isomerides by treatment with 2:6-dichloroquinone

chloro-imide, which converts *o*- and *m*-cresols into indophenols. Pure *p*-cresol, thus prepared from a commercial sample and afterwards purified by distillation, gave the boiling point (corrected) 202·3° C., which is 1·2° above the value commonly accepted. T. H. P.

Analysis of Mixtures of the Isomeric Toluidines. H. H. Evers and N. Strafford. (*J. Soc. Chem. Ind.*, 1927, **46**, 114–117.)—Existing methods for the analysis of the toluidines ignore the presence of the *m*-isomer, which is usually present in small amounts. Other objections to these methods are cited, including the fact that Schoen's method for the determination of the *p*-compound is not quantitative on account of the interfering action of the *o*- and *m*-compounds. The proportion of *m*- to combined *o*- and *p*-toluidines is determined by titration with a standard bromate solution, when the *m*-, *o*-, and *p*-isomers absorb three, two, and two atoms of bromine per molecule, respectively (*see* Callan and Henderson, ANALYST, 1922, **47**, 362). The *p*-isomer is determined from the comparison of the setting-point of a mixture containing, *e.g.*, 60 per cent. and 40 per cent. of pure *p*- and *o*-toluidines, respectively, with that of a mixture of 60 per cent. of *p*-toluidine and 40 per cent. of the sample. Complete reference curves correlating setting-point and composition are obtained by the gradual addition of pure *o*- to pure *p*-toluidine. The addition of the *m*-isomer in amounts usually present in such mixtures has no effect on the setting-point. A table of setting-points is given for mixtures of compositions up to 50 per cent. of each isomer. Determinations must be carried out on freshly prepared mixtures which have not previously been melted and allowed to solidify, or low setting-points are obtained. The *o*-toluidine is then determined by difference. J. G.

Inorganic Analysis.

New Method for the Determination and Separation of Metals by means of o-Oxyquinoline. R. Berg. (*Z. anal. Chem.*, 1927, **70**, 341–347.)—Copper and other metals may be precipitated by *o*-oxyquinoline, and a perceptible precipitate is obtainable from 0·008 mgrm. of copper. The precipitation is specific for copper, magnesium, zinc, cadmium and divalent iron in the presence of an alkaline solution of sodium tartrate. In the determination of copper an alcoholic solution containing 2 per cent. of *o*-oxyquinoline is added, drop by drop, till a yellow colour denotes a slight excess. The solution is warmed to 50 to 60° C., cooled, and the precipitate filtered off, washed with sodium tartrate solution (1 per cent.), with weak alkali, and then with pure water. The precipitate is dried at 110° C., and weighed; it has the composition $(C_9H_6ON)_2Cu$. Alternatively, the action of a known excess of a solution of iodine produces the compound $C_9H_7ON.I_2$, and the excess may be determined by titration with sodium thiosulphate solution. The maximum error of the method is 0·2 mgrm. for amounts of copper ranging from 2·5 to 90 mgrms. Other metals may be determined by precipitation in the presence of acetic acid or ammonia, and separations

on these lines have been devised. The accuracy in all cases depends on the degree of acidity or alkalinity. Copper cannot be separated from zinc by this method, but in the presence of magnesium it is removed by precipitation in acetic acid solution and the magnesium determined in the filtrate after the addition of ammonia. J. G.

Iodimetric Determination of the Antimonic Ion. A. Travers and Jouot. (*Compt. rend.*, 1927, **184**, 605–606.)—The reaction,

$$Sb_2O_5 + 4HI \rightleftharpoons Sb_2O_3 + 2I_2 + 2H_2O,$$

may be rendered complete in the direction from left to right by addition to the potassium iodide used of excess of concentrated hydrochloric acid. The acidity should be about 15 per cent. of hydrochloric acid, and about five times the theoretical quantity of potassium iodide should be taken. By this means the iodimetric determination of antimony in anti-friction alloy or type metal may be carried out in less than 30 minutes with an accuracy equal to that of the electrolytic method. Type metal may be attacked by hydrochloric acid containing 13 per cent. of bromine, pure lead itself being rapidly acted on by this reagent. T. H. P.

Simplified Determination of Molybdenum in Steel and Iron. E. Färber. (*Chem. Zeit.*, 1927, **51**, 171.)—In the method in which the molybdenum in iron or steel is separated as sulphide and this converted into the trioxide the double precipitation of the sulphide, practised in order to obtain the trioxide pure, may be avoided by the following procedure: From 1 to 2 grms. of the turnings are completely dissolved in a 400 c.c. beaker in hydrochloric acid (1·19), and the solution then treated carefully with 2 grms. of ammonium persulphate to dissolve any separated molybdenum and convert any tungsten present into tungstic acid. Ammonia solution is added to the filtered liquid until this is only just acid, hydrogen sulphide being passed into the boiling liquid for 20 minutes. After thorough settling, the precipitated molybdenum sulphide is transferred to an 11 cm. ashless filter and washed, first with hot dilute hydrochloric acid and then with hot water. The filter and precipitate are dried and ashed in a porcelain crucible, preferably by placing the crucible in a larger one and heating over a small Bunsen flame. The residue is weighed (A) and heated for an hour with 15 per cent. potassium hydroxide solution, which dissolves the molybdenum trioxide but leaves undissolved the copper, iron, etc., present as impurities. The contents of the crucible are transferred to a large beaker and diluted with about 150 c.c. of water, the liquid being heated to about 80° C. and filtered through an 11 cm. ashless filter. The residue on the filter is well washed with hot water, dried, and weighed (B) in a porcelain crucible. The amount of molybdenum, as trioxide, is given by (A – B). T. H. P.

Fractional Precipitation of Barium and Radium Chromates. L. M. Henderson and F. C. Kracek. (*J. Amer. Chem. Soc.*, 1927, **49**, 738–749.)—As a means of separating barium from radium, the fractional precipitation of the

chromates is comparable in effectiveness with the best results obtained by the fractional crystallisation of the mixed bromides.

The chromate method does not not lend itself readily to the construction of a crystallisation system, but it has the advantage of rapid enrichment by the use of comparatively inexpensive chemicals, and is applicable to relatively small quantities of material. Moreover, it may be used for recovering radium from radium-barium solutions too poor in radium to be concentrated economically by the chloride method. T. H. P.

Specific Reaction for Sodium. I. M. Kolthoff. (*Z. anal. Chem.*, 1927, **70**, 397–400.)—Zinc uranyl acetate is a specific reagent for sodium, giving a precipitate of the composition $(UO_2)_3ZnNa(CH_3CO_2)_9.9H_2O$. The reagent is prepared from warmed solutions containing (*a*) uranyl acetate 10 grms., 30 per cent. acetic acid 6 grms., and water to 50 grms.; and (*b*) zinc acetate 30 grms., acetic acid 3 grms., and water to 50 grms. The mixture is filtered a day after mixing. The solution to be tested (0·5 c.c.) is mixed with 4 c.c. of reagent; at a sodium concentration above 0·5 grm. per litre, an immediate precipitate is obtained; at one-tenth that concentration, the precipitate appears after 30 minutes. The reaction can be carried out in presence of copper, mercury (*ic*), cadmium, nickel, cobalt, aluminium, manganese, zinc, the alkaline earths, and ammonium, all at a concentration of 5 grms.: 1000 c.c. Potassium if over 5 grms.: 1000 c.c. is gradually precipitated; the test must be judged after not more than 15 minutes. The presence of 0·4 part of sodium in 100 of potassium can thus be proved. The reaction may also be carried out by mixing 2 c.c. of the solution to be tested with 2 of reagent and 2 of alcohol; 0·1 grm. of sodium per 1000 c.c. gives an immediate precipitate; at 0·025 : 1000, 10 minutes' standing is sufficient. The potassium concentration should be below 5 grms.: 1000 c.c., and the result must be ascertained after 10 minutes' standing. W. R. S.

The Accuracy of Argentometric Halogen Titrations. I. M. Kolthoff and L. H. van Berk. (*Z. anal. Chem.*, 1927, **70**, 369–394.)—The accuracy of the *potentiometric determination* of chloride and thiocyanate is 0·02 per cent.; the determination of bromide also is very accurate, whilst that of iodide is a little less so, due to the greater adsorptive power of silver iodide. *Mohr's method* gives accurate results for chloride and bromide when allowance is made for the excess of reagent required for the colour change; iodide and thiocyanate are not titratable. *Volhard's method* permits of the accurate determination of bromide, iodide, and thiocyanate if the liquid is strongly shaken at the end-point, so that the adsorbed silver is converted into thiocyanate. *Titration by Fajans' method* (ANALYST, 1923, **48**, 401) in neutral solution (fluorescein as indicator) is accurate; chloride solutions should be stronger than 0·005 *N*. Eosin is specially serviceable for bromide and iodide, as well as thiocyanate, and has the advantage that the titration can be carried out in weakly acid solution—up up to 0·1 *N*—but addition of sodium acetate is recommended in such cases. Large

amounts of electrolyte, which cause flocculation of the precipitate at the outset, render the process inapplicable. Iodides are conveniently titrated without indicator till the solution clears by shaking even in the presence of electrolytes.

W. R. S.

Argentometric Determination of Iodide in Presence of Choride. I. M. Kolthoff. (*Z. anal. Chem.*, 1927, **70**, 395–397.)—Iodide can be titrated in presence of chloride with the help of an indicator less strongly absorbed by silver iodide than iodide, but more strongly than chloride. Eosin was found serviceable in a solution containing 5 c.c. of 2*N* ammonium carbonate solution. The solution is titrated with silver nitrate till the silver iodide flocculates as a dark violet precipitate ; if chlorides are present the precipitate remains in colloidal suspension and the colour change takes place throughout the solution. The accuracy is 0·2 to 0·5 per cent. As little as 0·004 grm. of potassium iodide can be determined with an accuracy of 1 per cent. in presence of 1 grm. of potassium chloride. Bromides interfere. W. R. S.

Sources of Error in the Determination of Phosphoric Acid. J. M. McCandless and J. I. Burton. (*Ind. Eng. Chem.*, 1927, **19**, 406.)—Error in determining phosphoric acid by the molybdenum magnesium method may be introduced by some of the molybdenum being carried down in the course of the ammonium magnesium precipitation. If this precipitation is carried out in alkaline solution, much less molybdenum is co-precipitated than if carried out in neutral or acid solution. The presence of molybdenum can be shown by a hot digestion of the precipitate in 10 to 15 c.c. of 1:1 hydrochloric acid, followed by the addition of a few drops of sodium sulphide solution to the diluted acid solution. The intensity of the brown coloration is proportional to the amount of molybdenum present. If the magnesium ammonium phosphate precipitate containing small amounts of molybdenum is ignited over a Bunsen burner, the molybdenum remains with the magnesium pyrophosphate, but if ignited in a Gooch crucible, in a muffle furnace, or by a blast lamp at a white heat, it is volatilised and a pure precipitate is obtained. The most suitable salt to employ as a standard by which to test the accuracy of a method is microscosmic salt, $NaNH_4HPO_4.4H_2O$. This material is rarely supplied pure, and should be prepared in the laboratory. Another source of error is the magnesia mixture. If this is kept for some weeks, it is liable to attack the glass of the bottle, silica going into solution. It is best to make up the solution of magnesium and ammonium chlorides only, and to add the ammonia just before the solution is required. R. F. I.

Determination of Phosphorus in Alloys. B. Salkin. (*Ind. Eng. Chem.*, 1927, **19**, 416.)—Analysis, by the *aqua regia* method, of alloys containing high percentages of phosphorus (5 per cent., as in phosphorus-tin) gives low results owing to loss of phosphine. The usual method of overcoming this loss by absorption in nitric acid and bromine is slow and also dangerous. The following method is recommended :—A 300 c.c. conical flask is provided with a two-holed rubber

stopper. Through one hole is a tap-funnel connected with a source of compressed air (at 25 to 30 c.c. of water). The delivery-tube from the other hole is connected with a condenser, whereby the condensed liquid returns to the flask and the evolved phosphine passes on to an absorption-bulb containing a mixture of concentrated nitric acid and (excess of) bromine. A diagram of the apparatus is given. For the determination, 1 grm. of the alloy is placed in the conical flask and just covered with water. Into the tap-funnel is poured a mixture of 10 c.c. of concentrated nitric acid, 20 c.c. of concentrated hydrochloric acid and 10 c.c. of water. This mixture is run slowly into the flask, and the tap closed. The contents of the flask are then slowly heated to boiling, the flame is lowered and air blown slowly through the solution. After about 1500 c.c. of air have passed (15 to 20 minutes), the flame is removed and the apparatus disconnected. The liquids in the flask and in the absorption bulbs are mixed in a 500 c.c. beaker, boiled down to less than 150 c.c., cooled and diluted to the mark in a 250 c.c. graduated flask. Fifty c.c. of this solution are taken, and the chlorides and free chlorine removed by boiling for 5 minutes with 5 c.c. of a saturated solution of potassium permanganate. The necessary excess of oxides of manganese is filtered off, the filtrate boiled with sufficient sodium nitrate till decolorised, 15 c.c. of concentrated nitric acid added, and the boiling continued till all nitrous acid fumes are removed. Ten grms. of ammonium nitrate are added, the solution warmed to 70–80° C., and the phosphorus precipitated with 100 c.c. of ammonium molybdate solution. After the solution has stood for 4 hours (or over-night) the precipitate is filtered off in a tared Gooch crucible, washed with 100 c.c. of a solution containing 3 grms. of nitric acid and 3 grms. of ammonium nitrate, and finally with just sufficient water to remove the ammonium nitrate. The crucible is weighed after being dried at 110°C. Any arsenic present in the alloy is precipitated together with the phosphomolybdate. R. F. I.

Physical Methods, Apparatus, etc.

Laboratory Method of Determining the Starting Properties of Motor Fuels. W. G. Lovell, J. D. Coleman, and T. A. Boyd. (*Ind. Eng. Chem.*, 1927, **19**, 389.)—The starting properties of a motor-fuel are a complex function of its physical and chemical properties and of the temperature of its mixture with air and cannot be determined from distillation curves and dew points. A fuel that will give easy starting in a motor-engine is one which, when mixed with air, evaporates so completely that only a little of it is required to yield an explosive mixture. An apparatus is described which is designed for use on this principle. It consists of a closed bomb of about 300 c.c. capacity, placed in a thermostat and containing a high speed fan (2200 r.p.m.) for thoroughly mixing the fuel vapour with the air. To the shaft of the fan are attached two small cups for holding the fuel. For making a determination, the bath is set at the temperature desired, *i.e.*, at any point between −15 and 25° C.). A measured amount of the fuel to be tested is run into one of the cups in the bomb, which is

then closed with a cork. The fan is rotated for 2 minutes, after which the mixed gases are ignited by a continuous vibrating spark. If no explosion occurs, the bomb is cleaned out and dried and the process repeated with increasing amounts of fuel till the smallest amount that would give an explosion is found. Sufficient time must be allowed for the mixed gases to attain the temperature of the thermostat, the fan running during this period (*4 minutes at low temperatures*). The source of ignition must be kept constant. The most satisfactory procedure for determining the end-point is to observe the time that the vibrating spark had to be continued in order to give an explosion. For rich mixtures the time is practically instantaneous. As the mixture becomes poorer the time increases to 3 or 4 seconds, and finally there is a sharp point where further dilution of the mixture increases the time to 10 or 20 seconds. This abrupt break in the time of ignition curve is taken as the explosive limit, and was chosen because it is a definite and reproducible point. The results with this apparatus confirm those found by actual trial in motor engines. R. F. I.

Use of Anhydrous Perchlorates as Dehydrating Agents for Gases. G. F. Smith. (*Ind. Eng. Chem.*, 1927, **19**, 411.)—The most important properties in a drying agent are the following:—(1) High efficiency; (2) high absorptive capacity; (3) ready restoration of the exhausted material to its original condition without removal from the drying tower or tube; (4) ease of preparation; (5) stability and non-fusibility of the exhausted material at its temperature of dehydration; (6) inertness toward acid and alkaline gases; (7) moderate cost. All these properties are seldom possessed by one material. A mixture of 73·5 per cent. of anhydrous barium perchlorate and 26·5 per cent. of anhydrous magnesium perchlorate is satisfactory in all these respects. It is as efficient as concentrated sulphuric acid. A column of it (6 × 1 in.) is capable of drying air of 60 per cent. relative humidity at a rate of 1 litre per minute at 27° C. A bulk quantity of the exhausted material can be regenerated in trays with 10-mesh wire cloth bottoms and covered to a depth of $\frac{1}{2}$ to $\frac{3}{4}$ in., with a half-inch clearance between the trays, by being exposed to a temperature of 250° C. at 102 mm. pressure. An application for a patent has been filed. R. F. I.

Calculation of Flash Points of Blends of Lubricating Oils. E. W. Thiele. (*Ind. Eng. Chem.*, 1927, **19**, 259–262.)—The method is based on the principle that the reciprocal of the antilogarithm of one one-hundredth of the flash point (in degrees F.) is an additive property of the oil on a volume basis. Let F, F', F'', be the flash points of the constituents (in degrees F.), assuming that there are three constituents; x, x', x'', the volume fractions (0·01 of the volume per cents.) of the three constituents; and F_m the flash point of the mixture, then

$$Fm = -100 \log \left[x\left(10^{-\frac{F}{100}}\right) + x'\left(10^{-\frac{F'}{100}}\right) + x''\left(10^{-\frac{F''}{100}}\right)\right].$$

For example, suppose it is required to find the flash point of a mixture of 75 per cent. by volume of red oil (flash point 380°F.) and 25 per cent. of Pennsylvania

mineral oil (flash point 260°F.) : one one-hundredth of 380 is 3·80, and this is the logarithm of 6300, the reciprocal of which is 0·000159. Similarly, 2·60 is the logarithm of 398, and the reciprocal of this is 0·002515. Each of the quantities 0·000159 and 0·002515 can be found by one setting of a slide rule.

25 per cent. of 0·002515 =	0·000628
75 per cent. of 0·000159 =	0·000119
Total ..	0·000747

The reciprocal of this total is 1339, the logarithm of which is 3·13. Hence the flash point of the mixture will be 313 F. Tables are also given showing the flash points of mixtures of two oils, and these tables may be used for more complex mixtures by considering the various ingredients as added one at a time. W. P. S.

Reviews.

SEROLOGISCHE VERFAHREN DER NAHRUNGSMITTELUNTERSUCHUNG. (Serological Methods in the Investigation of Foodstuffs.) By PAUL MANTEUFEL. Handbuch der biologischen Arbeitsmethoden, Abt. IV, Teil 8, Heft 7, Lief. 203. pp. 1809–1918. Urban and Schwarzenberg, Berlin, 1926.

In this work Professor Manteufel presents, with a very minimum of theoretical digression, an account of the application of serological methods to the investigation of foodstuffs. The article is planned on straight-forward lines; in Part I the various methods and reagents are discussed in general terms, whilst in Part II their special application to the analytical study of different forms of food material is more closely considered. Discussion mainly concerns the differentiation and identification of animal proteins and more particularly those of larger food animals.

Present practice relies on three methods of study: viz. the precipitation test, the complement-fixation test and the anaphylaxis reaction, and in each case the procedure is methodically described, down to the smallest details of manipulation.

The precipitation test is very rightly offered as the method of first choice. The standard accepted for a satisfactory precipitating serum is that it should give a definite reaction with a 1:20,000 dilution of the homologous antigen, but should not react to heterologous protein above a 1:200 dilution. Since the sera usually employed for diagnostic work are prepared against blood serum proteins, the necessity of making due allowance for the organ specificity of tissue extracts is pointed out. While solutions of serum proteins should be standardised to the same content of coagulable protein as a 1:1000 dilution of fresh serum, extracts

of flesh and other tissues should be set at three times this concentration in order to maintain a sufficiency of species specific antigen.

The complement fixation reaction—so sensitive as a test for homologous protein—is, on account of its complexity and its susceptibility to non-specific influences, the least valuable of the methods at the disposal of the analyst. The test for analphylactic hypersensitiveness, actively or passively conferred, is far more reliable and may give definite results with material too weak or too much altered to respond satisfactorily to precipitating sera.

Besides these established methods the author discusses the possible value of three other tests. One of these, the Bordet conglutination test, merely substitutes another indicator reaction in the complement fixation test; it is difficult to see how this modification, so interesting in itself, can confer special practical advantage. More suggestive of future value are the attempts to utilise the differential distribution of the heat-resistant alcohol-soluble heterogenetic antigen of Forssmann to effect a "group diagnosis" among mammals either by means of a complement fixation reaction (Sachs-Georgi) or a flocculation reaction (Sachs-Guth).

The differentiation of the blood, flesh, bone and milk proteins are individually considered, and special sections deal with the more difficult problems of meat extracts, animal and plant fats and oils, egg and roe preparations and honey, in which the essential proteins are profoundly modified, are present in minute quantity, or are markedly non-specific in character. The article concludes with a section on the imperfectly investigated proteins of plants.

Among interesting points discussed are the facts with regard to "lacto-sera" and their value for the recognition of milk, and the peculiar reaction—wrongly called conglutination test—used by Mez in his studies of plant relationships.

The book offers little in the way of novelty, but unquestionably succeeds in giving a clear and comprehensive account of present knowledge of the serology of foodstuffs. If any adverse criticism is to be made it concerns the illustrations: one or two are poor, others are but little instructive, and almost all portray procedures and implements with which the general laboratory worker is well acquainted. One cannot but feel that some of the space so occupied might have been more usefully given to a few illustrative experiments drawn from the author's experience or from the literature.

P. Bruce White.

A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VII. By J. W. Mellor, D.Sc. Pp. vi + 977. London: Longmans & Co. 1927. Price 63s. net.

This volume comprises Chapters XLI to XLVIII of Mellor's invaluable treatise, in which titanium, zirconium, hafnium, thorium, germanium, tin, lead and the inert gases are discussed. The treatment accorded to these elements is somewhat irregular, and matter sometimes is found in the least expected places

and is absent from those paragraphs in which it would seem to be more relevant. The inclusion in the text of copious lists of names of investigators, with scarcely any indication of the way in which they may be considered to have advanced scientific knowledge, often makes it difficult to hold the sequence of the subject matter, and, without referring to the original papers, to obtain a satisfactory knowledge of some of the subjects treated in the volume. To some extent this difficulty is almost inevitable in a compilation of such mammoth, and yet necessarily limited, dimensions. It should be said, however, that the literature references are as complete as might be considered to be humanly possible, and, especially when it is remembered that Dr. Mellor alone is responsible for the treatise, one is bewildered at the efficiency with which these references have been collected and assimilated. The volume, as do the preceding ones, provides a veritable gateway to the literature, not only to that which is purely chemical, but also to much that lies almost exclusively in the province of physics and geology.

There are evidences, here and there, of hurried compilation, but this, perhaps, may be attributed to a natural desire on the part of Dr. Mellor to see his gigantic task accomplished. Thus in connection with the chemistry of zirconium, to which the reviewer has devoted some attention in recent years, it is found that the author sometimes deals at length with the interpretations of certain workers which have since been shown to be erroneous, and has lost sight of the later criticisms based on more recent work. No references could be found, for example, to the doubts which the reviewer has raised as to (*a*) the existence of the so-called "zirconyl" radicle $ZrO^{\cdot\cdot}$, (*b*) the amphoteric nature of zirconia both in solution and in the fused state, (*c*) the validity of the proof, afforded by Chauvenet's density determinations of zirconia combined with varying amounts of sulphuric acid, of the existence of certain definite basic sulphates of zirconium (*cf. J. Chem. Soc.*, 1925, **127**, 2124, 2140).

Observations were made on the nomenclature employed in an earlier volume, and the reviewer must apologise for criticising the unsatisfactory scheme to be found in the volume under review. One cannot help feeling that Dr. Mellor has become a slave to, and, indeed, a victim of, his system. For instance, it is not clear why a simple hydrated zirconia containing water shown by the formula $5\,ZrO_2.2H_2O$ should be written as $Zr_5O_8(OH)_4$, then as $Zr(O.ZrO.OH)_4$, and therefore (?) as $ZrO_4(ZrO.OH)_4$, and consequently to become entitled to the terrible name of *tetrahydroxy zirconyl zirconate.* An insoluble mass corresponding to approximately $K_2O(ZrO_2)_3$ is hailed as *potassium paratrizirconate.* The prefixes "ortho" and "meta" when used in connection with inorganic acids appear to have given Dr. Mellor some trouble. A basic thorium carbonate containing $ThO_2,CO_2,2H_2O$ and considered by Chauvenet, who described it, as being the normal "orthocarbonate," $ThCO_4$, of the hypothetical "orthocarbonic acid, H_4CO_4, is termed by Mellor "*thorium oxycarbonate*" and "*thorium metacarbonate.*" Incidentally no mention is made of the reviewer's work on the precipitation of thorium basic carbonate (*J. Chem. Soc.*, 1926, 125). According to Dr. Mellor $H_{14}P_4O_{17}$ is

"*orthotetraphosphoric acid*," a substance formed by the linkage of 4 molecules of $P(OH)_5$ through the elimination of 3 molecules of water. Although, on principle, $P(OH)_5$ should undoubtedly be regarded as the "ortho" acid, the term is invariably applied to H_3PO_4, and, in fact, the author himself uses it when referring to lead orthophosphate. Mellor calls $H_{10}P_4O_{15}$ "*deuterotetraphosphoric acid*," and further suggests that $PbHPO_4$ might be regarded as the salt of that acid. This is beyond the reviewer's comprehension. Again, a substance, $3K_2CO_3$, $2PbI_2,2PbO,2H_2O$ is set down as $3K_2CO_3,2Pb_2OI_2,2H_2O$, whence it becomes *potassium dioxytetraiodotricarbonatotetraplumbite*.

The reviewer fails to understand the purpose of the many structural formulae scattered throughout the book, as they appear to be based on no chemical properties, *e.g.* $SO_4.ZrO.SO_4.ZrO.SO_4.Zro.SO_4.ZrO.SO_4$

$$\dot{Z}rO\text{----------}O\text{----------}\dot{Z}rO,$$

In conclusion, it should be emphasised that these criticisms sink almost into insignificance when the merits and usefulness of the volume are taken into consideration.

HUBERT T. S. BRITTON.

VOLUMETRIC ANALYSIS. By C. H. HAMPSHIRE. 4th edition. Pp. 130. London: J. & A. Churchill. 1927. Price 7s. 6d.

This small manual, previous editions of which have already been reviewed in the pages of the ANALYST, is intended to provide instruction in the preparation and use of volumetric solutions by pharmaceutical and other elementary students. A greater number of estimations is contained in the present edition than in former ones, but, otherwise, little alteration has been found necessary.

The contents include acidimetry and alkalimetry, a chapter on indicators and sources of error, oxidation and reduction methods, and precipitation reactions, and the amount of material contained is relatively enormous when the size of the volume is considered, although ionisation and hydrogen ion concentration are wisely omitted. Not only are the usual titrations described, but the use of volumetric solutions in the evaluation of over a hundred pharmaceutical preparations is given and will add considerable interest to the student's work.

Throughout the text emphasis is rightly laid upon the relation between normal solutions and their hydrogen equivalent, and the descriptions of methods are concise, accurate, and expressed in such a manner that the conscientious student will meet with little difficulty in gaining a thorough and reliable knowledge of volumetric work.

The book has been admirably produced in every way and is singularly free from errors both in the text and also the index. Two items, only, deserve adverse criticism: one on p. 32, where the startling statement is made that "(Rochelle salt) is converted on incineration into a mixture of potassium and sodium,"

and the other on p. 66, in which a Bunsen valve is depicted with a rubber tube of very unusual shape. The author is evidently well acquainted with the requirements of the student, and has produced a well written volume which undoubtedly deserves a wide circulation.

T. J. WARD.

A STUDENT'S MANUAL OF ORGANIC CHEMICAL ANALYSIS, QUALITATIVE AND QUANTITATIVE. By J. F. THORPE, F.I.C., F.R.S., and M. A. WHITELEY, D.Sc., F.I.C. Pp. x + 289. London: Longmans, Green & Co. Price 9s. net.

The first edition of this book was published in 1925 and reviewed in the ANALYST in January 1926 (Vol. LI, No. 598, p. 55). That a second edition should appear so quickly is, in itself, excellent confirmation of the opinions previously expressed concerning it.

The new edition differs from the old in that an appendix of 39 pages, entitled "New Methods of Organic Analysis," by H. Ter Meulen and J. Heslinga, has been added. These methods cover the usual elements met with in organic compounds and include the determination of *oxygen*. The novel feature of the work is the employment of catalysts. In the case of carbon and hydrogen, manganese dioxide is used, and in all other cases methods involving catalytic hydrogenation are described. Modifications for every contingency are given, and, since most of the processes are rapid, they are likely to be much used in the future. The apparatus required is very simple, being, for the most part, easily made up from ordinary laboratory materials.

The addition of this section has made Thorpe and Whiteley's book more useful than ever, and the reviewer has no hesitation in recommending it to all engaged in chemistry.

HAROLD TOMS.

CHEMISTRY OF THE OIL INDUSTRIES. By J. E. SOUTHCOMBE. 2nd edition. Pp. 224. London: Constable & Co., Ltd. 1926. Price 12s. 6d. net.

The first edition of this book was published in 1913, and was reviewed in the ANALYST (1913, 38, 445.)

The scope of the book, which deals with both the mineral oil and the fatty oil industries, remains the same as in the previous edition; the general arrangement of the subject matter and a large proportion of the text have not been altered. Whilst most of the chapters in the new edition contain but little new matter, that dealing with mineral oils has been largely rewritten. A chapter dealing with the "Theory of the Colloidal State" (an addition suggested in the previous review in this journal) has been added, together with a somewhat incomplete bibliography.

The new edition contains many statements and opinions which, while sound in 1913, have now become out of date and have not been removed or replaced.

Many of the developments of the last thirteen years either are not mentioned or are dealt with, inadequately. Thus, the author has devoted to the catalytic hydrogenation of oils two short passages occupying about ten lines in all, and, of these, one is misleading. He makes no mention of the chemistry of the process or of the very extensive use of hydrogenated oils in lard substitutes and margarine, although sections on the composition of such substitutes are included.

The chapter on "Analytical Methods" has been reprinted, word for word, from the first edition; as was remarked in the review of that edition, "the methods savour more of the lecture room than of the technical laboratory"; the value of this chapter would have been greatly enhanced by revision. Of the methods included, one, described as the Reichert-Meissl process for the determination of soluble volatile fatty acids, is actually the Reichert-Wollny process; and a second, attributed by the author to Holde, for the detection of mineral oils in vegetable oils, is a test based by the author on the surprising and erroneous statement that "mineral oils are insoluble in 96 per cent. alcohol, but all fats dissolve fairly readily." Holde's test, which is not described, is based on the principle that when vegetable oils are boiled with alcoholic potash, an alcohol-soluble soap is formed, whereas mineral oils remain unchanged and insoluble under the same treatment.

The book contains an example of the manner in which misleading statements are copied from one book to another. A table on p. 77 has been abstracted from a similar table in Ubbelohde. The figures for the proportions of fat in copra and in palm fruit are reversed in Ubbelohde and remain reversed in both editions of Southcombe; it may further be mentioned that, of the four figures in question, one has been incorrectly copied.

K. A. WILLIAMS.

CHEMISTRY AND MANUFACTURE OF WRITING AND PRINTING INKS. A List of References in the New York Public Library. Compiled by W. B. Gamble. Pp. 105. New York, 1926.

Although this pamphlet is intended primarily to give information as to the contents of a particular library, it is so well arranged and contains so much specialised information in a condensed form that it could also be used as a valuable appendix to any book on the manufacture of writing and printing inks or their pigments.

The first section, of 37 pages, contains 728 references to books and papers in scientific and technical journals, arranged alphabetically under the author's name, and giving in many cases a brief note on the subject matter. The ground covered is very wide, and the references date back to the seventeenth century. Naturally the American references are very numerous, and it is probable that from no other source could one readily obtain information on the papers which have been published in the American technical press.

The following section, of 47 pages, gives lists of patents, classified chronologically under the names of the different countries, and giving, in each case, a brief note as to the trend of the invention. This section is followed by an alphabetical list of the patentees, and finally there comes a very full subject index.

The general impression gained by a study of these pages is best conveyed by echoing the words of Mr. H. Lydenberg, who has written the introduction: "No one but the specialist would ever dream that so much has been written about ink, and certainly specialist and outsider, connoisseur and casual enquirer, will rejoice that this key to the literature of ink has been so admirably wrought and so conveniently put into his hand."

EDITOR.

Publications Received.

THE ART AND PRINCIPLES OF CHEMISTRY. By H. E. ARMSTRONG. E. Benn, Ltd. Price 15s.

ANCIENT EGYPTIAN METALLURGY. By H. GARLAND and C. O. BANNISTER. Charles Griffin & Co., Ltd. Price 12s. 6d. net.

LUBRICATION AND LUBRICANTS. By L. ARCHBUTT and R. M. DEELEY. Charles Griffin & Co., Ltd. Price 36s. net.

SPECTROSCOPY. By E. C. BALY. Longmans, Green & Co., Ltd. Price 18s. net.

SELENIUM: A LIST OF REFERENCES, 1817—1825. Compiled by M. F. DOTY. The New York Public Library.

THE DYEING OF TEXTILE FIBRES. By R. S. HORSFALL and L. G. LAWRIE. E. Benn, Ltd. Price 18s. net.

THE CHEMISTS' YEAR BOOK, 1927. Edited by F. W. ATACK. Sheratt & Hughes, Manchester. Price 21s. net.