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The Identification of Common Edible Sea Fish (with Demonstration)*

By C. HATTERSLEY (Chief Inspector, Fishmongers' Company)

(Demonstrated at the Joint Meeting of the Society with the Food Group of the Society of Chemical Industry, November 14, 1934)

THE distinctive characteristics of twenty-two species of common edible sea fish were demonstrated on actual specimens. The following are among the most important features to be studied:

COD.—The body of the cod is thick and rounded near the head, but tapers off suddenly towards the tail. The fish is of a greenish or brownish-olive colour with numerous yellowish or brown spots. It has a white lateral line, the upper jaw is large, and there is a barbel on the chin. There are 3 dorsal, 2 pectoral, 2 ventral (jugular), and 2 anal fins.

HADDOCK.—This is similar to the cod, but is smaller and may be distinguished by a black lateral line and a large blackish spot above the pectoral fin—the so-called finger-and-thumb marks. It has a small barbel on the chin. The colour is darker than that of cod, and, when first caught, the fish is of a beautiful bronze colour. It has 3 dorsal, 2 ventral, 2 pectoral, and 2 anal fins. The scales are rather large.

WHITING.—This is smaller than the haddock; the head and body are compressed; the deepest part is at the vent, which is opposite the middle of the first dorsal fin; eyes moderately large; there is no barbel on chin; the scales are small and silvery; the skin is of a dusky yellow colour, the sides paler and the belly silver-white; there is a black spot on the upper side of the root of the pectoral fin. There are 3 dorsal, 2 pectoral, 2 ventral, and 2 anal fins.

HAKE.—This is another elongated fish. It has no barbel but, unlike the ling, has large scales and a large mouth with exceedingly sharp teeth. The colour is dark grey on the back and slightly lighter on the belly. It has 2 dorsal, 2 pectoral, 2 ventral, and 1 anal fin.

* The Ministry of Agriculture and Fisheries has drawn up a list (Fisheries Notice No. 23) of the names under which it is recommended that sea fish should be sold to the public. Reference to this will be made in the March issue of THE ANALYST.—EDITOR.

COALFISH.—This is similar in size to the cod, of a dark slate-blue colour, almost black on the back and sides, graduating to grey on the belly; the scales are large. It has no barbel. The lower jaw is slightly longer than the upper. A white lateral line is shown, and there are 3 dorsal, 2 ventral, 2 pectoral, and 2 anal fins. The usual length is 2 to 3 feet.

POLLACK.—This is similar to coalfish, and is of a dull green colour; belly greyish-white.

LING.—This is an elongated fish with very minute scales and two dorsal fins, the edges of which are tinged with grey; the first is high and short, the second very long, extending almost to the tail. It has a long barbel on the chin. The colour is usually grey on back with white belly.

CATFISH.—The head is removed and the fish skinned, and it is then largely sold as "rock salmon," especially by fish fryers. If exposed in its natural state with the head on, and labelled "Catfish," it would be unsaleable. When skinned it is pink.

DOGFISH.—This is sold and used in frying shops as "flake." It is so called because flakes are distinctly marked all down the body. It is a member of the shark family.

BRILL AND TURBOT.—These are very much alike. The turbot is round and has tubercles on the back, which are absent from the brill.

PLAICE AND DABS.—Plaice can always be identified by the spots on the back. Dabs, which are sometimes sold as plaice, have very much the same shape, but have no spots. The dab is very rough, whilst the plaice is smooth.

LEMON SOLE.—This is very like the dab. If in doubt, one should turn the fish dark side up and look at the lateral line. The line on the dab takes a sharp turn; also, the skin is rough, whereas that of lemon sole is smooth.

SOLE OR DOVER SOLE.—The skin is very dark on the back, very rough, and has a small black speck just at the top of the ventral fin. A useful fact in connection with sole is that, as a rule, it is cooked with its head on, and can then be identified by its curved mouth; hence, if served as "grilled sole" with only half a head, it may be looked upon as suspicious; it may possibly be a witch.

WITCH.—This is often substituted for sole or lemon sole. Lemon soles are whiter than witch. Witch is rather coarse on the front; rather grey instead of white.

MEAGRIM.—This and witch are the only two flat fish not distinctly white in front; they are rather greyish-white. Witch has a small head, small mouth and straight lateral line. Meagrim has a large head, large mouth and curved lateral line.

HAKE, POLLACK AND HADDOCK.—In distinguishing between these species the shape must be taken into consideration. The cutlets from the hake are circular, whilst those from the haddock are oblong; there are also differences in colour, pollack being not quite white, whilst hake is perfectly white. Pollack has only a faint lateral line on the skin, whilst the lateral line on the haddock is dark.

FISHMONGERS' HALL
LONDON, E.C.4

DISCUSSION

Replying to questions, Mr. HATTERSLEY said that *uss* was another name for dogfish. *Roker* or *thornback* was of the skate family, but was very heavily thorned on the back. *Lythe* was a local name for *torsk*. *Pouting* was one of the whiting family, but it had a very long barbel on the chin, which was absent from the whiting; it was also much broader in the body. *Flounder* was similar to plaice; it had the same shape, but was distinguished by having sharp spines on the lateral line, and also round the fins. *Bass* was sold in shops as "Salmon Bass." It looked very much like salmon, but the scales were more prominent, and the dorsal fin had five very sharp spines. In colour it was rather grey, graduating to silver. The term "*blue halibut*" had reference to the colour of the upper surface; some were bluish-black, whilst others might be grey-black, according to the grounds where they were caught. *Sardines* and *pilchards* were practically the same fish. When it grew beyond 4½ inches a sardine became a pilchard.

It was possible to distinguish between different fish after they had been skinned and filleted, but it required life-long experience to do so.

The difference between "right-handed" and "left-handed" fish depended upon the position of the eyes when viewed along the fish from the head; thus dab was "right-handed" and meagrim "left-handed." A set of fish scales was kept at Fishmongers' Hall, and when any doubt was raised regarding fish the scales were compared with the standards under the microscope.

Prosecutions had been instituted by the Middlesex County Council against shopkeepers for the substitution of fish. For example, haddock and pollack had been sold as hake, and cod fillets were sometimes sold as "hake" fillets. There was also the possibility that catfish might be filleted and substituted for other fish.

The Composition of Fish Pastes

BY H. E. COX, D.SC., PH.D., F.I.C.

(*Read at the Joint Meeting of the Society with the Food Group of the Society of Chemical Industry, November* 14, 1934)

ALTHOUGH there is recorded in our literature a fair amount of information about meat pastes and potted meat, there is very little on the subject of fish pastes from the point of view of composition. In view of the possible extension of standards and regulations, it seems worth while recording what has been observed as a result of the analysis of a fair number of samples sold in London. Fish pastes have been the subject of regulation with regard to preservatives in most countries, but only in a few in respect of composition or such matters as cereal additions. The addition of farinaceous material, usually bread, is fairly general, though by no means universal, but sometimes the quantity is so large as to amount to dilution or filling. Where limits have been enacted, as in Canada and Switzerland, 5 per cent. of dry starch is general, and in other countries, such as the U.S.A., Belgium, Italy, Australia and New Zealand, a declaration of addition is required.

Fish pastes are essentially factory products, seldom made at home, so that in approaching the question of what they ought or ought not to contain, one

cannot start from old-fashioned recipes, and regard must be had to factory conditions of supply, price, transport and processing. Dietetically they are more of a relish than a staple article of diet intended to serve as a meat ration, as a sausage may be. It is difficult, or often impossible, to determine their real composition by analysis, and the named fish is often merely the one giving the dominant flavour. It will, however, be generally agreed that fish pastes ought to be predominantly fish, and ought not to contain excessive proportions of diluents such as water, bread or salt.

For the purposes of the analyst, fish and fish products are conveniently divided into four groups: (i) Fatty fish; (ii) non-fatty fish; (iii) salted fish; and (iv) crustaceans. The percentages of fat and nitrogen in these groups are fairly characteristic and serve as a basis for the calculation of the proportion of fish in the fish pastes made from them. Unfortunately, there are no known methods for determining the identity of fish in a cooked paste, though careful microscopic examination, together with determination of the chemical composition, often affords useful indications. The microscopic appearance of any scales or bits of shell or bristles may help.[1] The following table shows the average composition of the commoner types of fish, of which salmon is much the most important from the present aspect. The data are collected from various sources—Plimmer, König, Atwater and Bryant—together with analyses of my own; all the figures refer to the edible parts of the fish.

TABLE I

	Water Per cent.	Fat Per Cent.	Protein Per Cent.	Ash Per Cent.	Salt Per Cent.	Nitrogen on fat-free basis Per Cent.
FATTY FISH						
Herring ..	72·5	7·1	19·5	1·5	0·3	3·4
Mackerel ..	73·4	7·1	18·7	1·2	—	3·2
Salmon* ..	66·6	10·5	21·5	2·0	0·6	3·9
Sprat ..	66·8	14·5	17·1	1·8	—	3·2
Sardine ..	58·5	8·0	20·5	9·5	—	3·6
NON-FATTY FISH						
Cod	82·6	0·4	16·5	1·2	0·2	2·6
Haddock ..	81·7	0·3	17·2	1·2	0·2	2·7
Hake	83·1	0·7	15·4	1·0	—	2·5
Whiting ..	80·4	0·2	17·7	1·1	—	2·8
SALTED FISH						
Anchovy ..	62·5	8·3	20·9	—	[7 to 20]	3·6
Bloater ..	64·0	14·0	19·0	2·0	0·9	3·6
Kipper ..	61·0	8·5	20·5	6·0	4·9	3·6
CRUSTACEANS						
Crab	73·6	0·2	22·4	2·7	0·3	3·6
Prawn ..	71·2	1·3	22·8	5·2	0·3	3·6
Lobster ..	71·5	1·0	20·7	3·4	—	3·3
Shrimp ..	70·0	0·9	22·0	6·8	1·5	3·6

* As canned.

Pacific salmon are said to be richer in fat than Atlantic salmon.

In all cases protein means nitrogen multiplied by the conventional factor, 6·25. Usually the analysis of fish in these terms adds up to something rather less

than 100 per cent., and the presence of small quantities of glycogen or other carbohydrate has been reported in many cases. Starch is never found as a natural constituent, so that, apart from any minute quantity due to condiments, its presence in fish paste always indicates bread or other filler. The amount of salt in anchovies, kippers and bloaters is apt to vary widely, and sometimes anchovy or bloater paste will contain quite large additions of salt. The following tables set out the analytical results obtained with a number of fish pastes; where I have analysed an adequate number of different brands the maximum, minimum and average are shown, but with other varieties, for which only one typical result is given, the figures are less representative.

TABLE II

	Salmon and shrimp 16 Samples			Bloater 9 Samples		
	Max. Per Cent.	Min. Per Cent.	Average Per Cent.	Max. Per Cent.	Min. Per Cent.	Average Per Cent.
Water ..	68·04	57·58	63·8	59·26	45·00	55·6
Fat ..	11·73	7·56	9·3	16·86	7·80	12·0
Protein ..	20·21	16·46	18·2	23·06	19·31	20·1
Ash ..	6·22	2·96	4·0	9·31	4·29	6·7
Salt ..	4·50	1·60	2·0	7·15	2·50	4·8
Starch ..	8·68	None	4·2	12·30	None	4·0

TABLE III

	Anchovy 9 Samples			Sardine and tomato	Salmon and anchovy
	Max. Per Cent.	Min. Per Cent.	Average Per Cent.	Per Cent.	Per Cent.
Water	65·60	38·12	55·7	60·39	63·02
Fat	38·13	0·90	12·1	9·60	9·12
Protein ..	22·98	17·60	20·6	18·95	14·04
Ash	16·70	4·01	7·1	3·35	5·32
Salt	14·20	3·32	5·9	Sugar 7·73	—
Starch ..	12·7	Absent	2·5	None	8·50

TABLE IV

	Lobster Per Cent.	Crab Per Cent.	Prawn Per Cent.	Shrimp Per Cent.
Water	68·77	66·70	66·20	64·72
Fat	9·83	5·19	8·56	11·50
Protein	15·53	18·79	21·60	18·37
Ash	3·10	2·56	3·98	2·99
Salt	1·02	0·60	1·70	1·82
Starch	3·05	6·76	None	2·50

Besides the main ingredients shown, small additions of pigments, such as bole, or of artificial dyestuffs, are fairly common. In my observation, fish pastes

which contain large proportions of starchy matter and water do not keep so well when the pots are opened, but are rather susceptible to mould growth. Preservatives are, of course, prohibited in this country, and so are not found, except that an occasional trace of boric acid may be detected if shrimps or other fish have been dusted therewith, and faint traces of formaldehyde may arise from natural causes.[2] One other abnormality in fish pastes is the presence of minute crystals of magnesium ammonium phosphate in the form of struvite, which is liable to be mistaken by the customer for glass. I have found these quite often in canned crayfish, shrimps and lobster. Manley[3] records their presence in tinned salmon. They may be as much as 5 mm. in length.

The calculation of the approximate composition of the paste is not difficult when the identity of the fish used is known; without such knowledge one can only proceed on the basis of probability fortified by the name on the label. The method is an extension of the lines adopted by Stubbs and More[4] for the determination of the proportion of meat in sausages.

The starch percentage, multiplied by 1·7, gives moist bread containing 40 per cent. of water and 1 per cent. of nitrogen. The nitrogen found, less 1 per cent. of the bread, multiplied by 100 and divided by the nitrogen per cent. in the fat-free fish used, gives the fat-free fish, to which must be added the fat found if its amount be not in excess of that natural to the percentage of fish indicated. When there is much fat, it is desirable to examine it in detail to ascertain its nature and origin. If there is no indication of the addition of butter or other foreign fat, any excess usually indicates the use of a fatty-fish basis such as salmon, which is common in crab, lobster and shrimp pastes. The proportions of salt and water natural to the fish are calculated from the fish basis, and any excess is noted.

As salmon is the commonest basis in mixed pastes, it is convenient and approximately correct to take its composition as the starting-point in attempting to calculate the ingredients of a mixture. The proportion of fat present helps in this direction; for example, in the shrimp paste shown there is much more fat than is found in shrimps, and it agrees approximately with that in a salmon basis. In another case, anchovy paste contained only 0·9 per cent. of fat, so that not only could there be but little anchovy in it, but the basis must have been a non-fatty fish of which the nitrogen basis is about 2·6 or 2·7. Two instances will show what sort of result may be expected. The crab paste shown in Table IV contains 5·2 per cent. of fat, so that it evidently contained a basis of nearly 50 per cent. of fatty fish—salmon; hence the nitrogen basis may be taken at, say 3·7, instead of 3·6 for shrimp or 3·9 for salmon. The starch percentage (6·76) is equivalent to 11·5 per cent. of bread, and so accounts for 0·11 per cent. of nitrogen and 4·5 per cent. of water. The nitrogen, less 0·11, is 2·90 per cent., which corresponds with 78·4 per cent. of fat-free fish or 84 per cent. of total fish, including 67 per cent. of water. Thus the composition works out at:

Fish	84	per cent.
Bread	11	,,
Added water	5	,,
	100	,,

Similarly, the composition of a salmon and shrimp paste giving the analytical data shown in the average in Table II can be calculated on a nitrogen basis 3·8, and corresponds to:

Fish	85	per cent.
Bread	7	,,
Added water	5	,,
Added salt	1	,,
	98	,,

These methods of calculation are put forward only tentatively, with the realisation that they are imperfect, and would be vitiated by a variety of circumstances. It is hoped that before long someone will discover a method which will enable us to identify and estimate any particular kind of cooked flesh.

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11 Billiter Square
London, E.C.3

Discussion

The Chairman (Dr. L. H. Lampitt) said that the subject of this paper was obviously one of intense interest, and one on which there was only very meagre information available. As Dr. Cox had already pointed out, certain pastes contained more than the amount of fat consistent with the type of fish used, but the possibility that it was essential to add fat, in order to obtain the desired palatability and consistence, must always be considered in connection with a product which was sold virtually as a luxury and not for its food value.

Professor J. C. Drummond suggested that the new technique for examining by adsorption would probably enable one to identify the pigments of the fish used in the paste. Much work had been done on the subject by German chemists, and he thought that in some cases the process would be very simple. It might, for instance, be possible to distinguish in this way between the pigments from the salmon and the anchovy. Quite small amounts of hydrocarbon and related carotinoid pigments could now be separated from oils by this method, and it might be possible by this means to differentiate certain fish.

Mr. C. E. Sage remarked that the difference in price between various fish pastes depended largely upon the market value of canned goods. *Real* shrimp extract was sold at 15s. per lb. The difference in price between fresh and canned Alaska salmon enabled the manufacturers of salmon paste to make an immense profit. When it was a question of cheapness one had to keep a careful watch on these products, and frequently the analyst was the only safeguard between the manufacturer and the consumer. The results put before them by Dr. Cox would enable them to form an opinion regarding some of the products upon which analysts had to report.

Mr. Morgan asked what would be the effect on the calculation of the composition if soya flour were used as a filler instead of ordinary bread.

Mr. J. W. Black asked whether Dr. Cox had been able to compare actual formulae with calculated formulae?

Mr. JOHN EVANS asked why the filler had been calculated as bread. Surely, manufacturers would be much more likely to use rusks.

Mr. STEVENSON asked if Dr. Cox had determined the copper-contents, especially in pastes made from crustaceans, the blood of which contained large amounts of copper and which were usually killed by boiling, so that no blood was lost.

Mr. T. MACARA asked if the figures used in the calculations had been compared with those of a number of the natural products. He was quite sure that there must be a wide variation in the composition of fish, and just as variation in pork affected the calculation of the composition of sausages, so variation in the fish must affect the calculations in the case of paste. He agreed with Dr. Lampitt that the manufacturer must add material to make the article spread well, to have a nice flavour and generally to be appetising, and he thought that these things should be kept in mind when dealing with a manufactured product. With regard to remarks made about fish paste being a profitable line—a good deal too much was made of this—the price indicated the product and an article would practically always find its true level of price in the market.

Dr. COX, replying, said that he had no experience of the method mentioned by Professor Drummond, but would be very glad to have details of it. He had not come across the *real* shrimp paste to which Mr. Sage referred. With regard to the different fillers which had been mentioned by Mr. Evans and Mr. Morgan, he thought that bread was the most usual, but it would be quite simple and appropriate to calculate the results in terms of rusks or like material, if one so desired. Soya flour in any substantial quantity would disturb the protein in relation to the other constituents, and he thought would be detectable. He agreed with Mr. Macara about the wide variations possible in the composition of fish, but surely one could only take averages as a basis of calculation. It would be much better to base calculations on fat and protein percentages rather than on traces of impurities, such as copper, which might be picked up from pans or other utensils.

Notes on Fish Pastes

BY C. H. MANLEY, M.A., F.I.C.

(*Read at the Joint Meeting of the Society with the Food Group of the Society of Chemical Industry*)

FOLLOWING the suggested standard put forward by Manley and Sutton[1] for potted meat, in which a maximum water-content of 70 per cent., together with the exclusion of starch, were advocated, it was felt that similarly, in a product sold as potted salmon, starchy filler should also be excluded.

Accordingly an attempt was made in the Leeds police court on May 5th, 1931, to emphasise the distinction between "potted salmon" and "salmon paste."[2]

A sample of food sold by a shopkeeper as "potted salmon" was found on analysis to contain 80 per cent. of salmon and 20 per cent. of a starchy filler, the proportion of the latter being calculated from a 6·6 per cent. anhydrous starch-content, 33 per cent. being taken as an average total solid figure for the starchy filler used. (Owing to the swelling of the grains during cooking it was not possible to identify the particular starch present.) The percentage of salmon, *viz.* 80 per

cent., calculated from the protein-content, supported the figure obtained for the starchy filler.

That a distinction should be drawn between the two products was admitted by the Stipendiary Magistrate, who dismissed the summons under the Probation of Offenders Act on payment of costs, defendant not having made the sample and having charged only the commercial rate for salmon paste, and not that for potted or tinned salmon.

Whilst one might reasonably expect to find a certain proportion of starchy filler in products sold as fish paste, it is significant that one well-known manufacturing firm last year published on a full-page advertisement in a London newspaper an analysis of its salmon and shrimp paste, from which starch apparently was excluded, the fish-content being given as 97 per cent., and the remaining 3 per cent. as butter and seasoning.

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86, SHAFTESBURY AVENUE
ROUNDHAY, LEEDS.

The Detection and Determination of Triethanolamine

BY H. RONALD FLECK, A.I.C.

THERE does not appear to be any published method for the determination of triethanolamine in toilet creams and emulsions. Compounds suitable for identification have been described by Jaffé[1], who prepared the complexes $(CH_2OH.CH_2)_3NH.BiI_4$, m.p. 193° C., and $(CH_2OH.CH_2)_3NH.SbI_4$, m.p. 174° C. The reaction of triethanolamine with cobalt salts in ammoniacal solution has been used as a test for the base by Garelli and Tettamanzi.[2]

In the routine analysis of creams in which a fatty basis is incorporated with water, the material is saponified and evaporated to dryness with lime, and the powdered residue is extracted with boiling absolute alcohol. The alcoholic extract, on evaporation, yields a viscous residue containing any triethanolamine, glycerol, or ethylene glycol which may have been present in the original material.

In the course of the present work it was found that commercial triethanolamine gave with hydriodic acid of constant boiling-point, a white crystalline substance which agreed with the composition $(CH_2OH.CH_2)_3N.HI$, and contained 53·6 per cent. of the base. This compound, on crystallisation from absolute alcohol, melted sharply at 169° C., the m.p. being unaltered by further recrystallisation. The hydriodide is somewhat soluble in ethyl alcohol, but practically insoluble in *iso*-propyl alcohol. The small solubility in this solvent has been determined and found to be 1 mg. per ml. at room temperature.

The following method based on these observations has been worked out:

METHOD.—An accurately weighed portion (about 0·5 g.) of the viscous residue from the alcoholic extraction described above is evaporated to dryness with 0·5 ml. of constant-boiling 57 per cent. hydriodic acid and 5 ml. of water in a glass dish. The residue is stirred with 5 ml. of pure *iso*-propyl alcohol, transferred to a 1.G.3 sintered glass crucible, and washed three times with 5-ml. portions of the alcohol, the crystals being sucked as dry as possible after each washing. The crucible and contents are dried to constant weight at 100° C., and a correction of 1 mg. for each ml. of *iso*-propyl alcohol used in the transference and washing of the crystals is applied. The m.p. of the product (169° C.) serves to identify triethanolamine. The weight obtained, multiplied by 0·536, gives the weight of triethanolamine present.

The method was tried on commercial triethanolamine, and also on triethanolamine purified as follows:

To about 20 g. of the base, dissolved in 50 ml. of 95 per cent. ethyl alcohol, were added 40 g. of 57 per cent. hydriodic acid. The resulting crystals were collected and recrystallised three times from 95 per cent. ethyl alcohol. A weighed quantity was dissolved in water and the exact amount of freshly precipitated silver oxide required to combine with the hydriodic acid in the compound was added. The mixture was well shaken for some time and filtered from the silver iodide. The filtrate was evaporated to dryness with a small amount of lime, extracted with absolute alcohol, and dried to constant weight at 50° C. *in vacuo*.

Results of typical experiments on this purified material were:

Pure triethanolamine taken g.	HI used ml.	Weight of hydriodide g.	Triethanolamine found g.
0·2663	0·5	0·4963	0·2660
0·5228	1·0	0·9746	0·5224

COMMERCIAL TRIETHANOLAMINE.—Commercial triethanolamine usually contains small amounts of the mono- and di-ethanolamines, together with some water. To study the effect of the mono- and di-substituted amines on the precipitation of the hydriodide a commercial sample was carefully fractionated *in vacuo*, in order to obtain the lower-boiling fractions. These were refractionated to give nearly pure mono- and di-ethanolamines, having the following constants:

	Approx. mol. weight	$n_D^{20°}$
Monoethanolamine ..	65·7	1·4445
Diethanolamine ..	99·4	1·4702

When each of these substances was tested by the method the material was entirely soluble in *iso*-propyl alcohol and no crystals were obtained. A mixture of these two products with the purified triethanolamine described above, gave the following result:

Mono-	di- ethanolamine	tri-	Weight of hydriodide obtained g.	Weight of triethanolamine found g.
0·0624	0·1150	0·3020	0·5626	0·3015

From this it is clear that the presence of mono- and di-ethanolamine does not interfere with the determination.

Commercial triethanolamine (4·3554 g.) was dissolved in water, and the solution was diluted to 100 ml.; 10 ml. were used for each analysis, the following weights of hydriodide being obtained:—(*a*) 0·7124 g., (*b*) 0·7258 g., (*c*) 0·7320 g., (*d*) 0·7100 g. Mean of 4 determinations: 0·7200 g. of hydriodide. The sample therefore contained 88·6 per cent. of triethanolamine.

The method gives moderately satisfactory results when glycerol or ethylene glycol is present, as the following figures show:

DETERMINATION IN THE PRESENCE OF GLYCEROL.—Varying weights of the purified base were mixed with known weights of glycerol, and the mixtures were dissolved in water and analysed. The results were as follows:

Weight of triethanolamine taken g.	Weight of glycerol taken g.	Base Per Cent.	Weight of triethanolamine found g.	Error Per Cent.
0·7597	0·2462	75·3	0·7527	−0·9
0·3859	0·4560	45·8	0·3903	+1·1
0·3859	0·9120	29·7	0·3751	−2·7
0·3859	1·3680	21·8	0·3696	−4·2
0·2348	2·5276	8·5	0·2266	−3·5

DETERMINATION IN THE PRESENCE OF ETHYLENE GLYCOL.—Varying weights of the pure base were mixed with known weights of pure ethylene glycol, and the mixtures were dissolved in water and analysed. The results were as follows:

Weight of triethanolamine taken g.	Weight of glycol taken g.	Base Per Cent.	Weight of triethanolamine found g.	Error Per Cent.
0·8043	0·2362	77·3	0·8011	−0·4
0·6208	0·3886	61·5	0·6170	−0·6
0·4335	0·6336	40·6	0·4210	−2·8
0·2640	0·7454	26·15	0·2587	−2·0
0·1970	1·8635	9·56	0·1903	−3·4

The method has also given satisfactory results with solutions of triethanolamine stearate and oleate, since these are decomposed by the hydriodic acid, with the production of triethanolamine hydriodide and the corresponding fatty acid, which is soluble in the *iso*-propyl alcohol.

I wish to thank Dr. A. M. Ward for his interest and helpful criticism during the course of this work.

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SIR JOHN CASS TECHNICAL INSTITUTE
JEWRY STREET, LONDON, E.C.

A new Method for the Colorimetric Determination of small Quantities of Iodide in presence of other Halides

By A. C. BOSE, Ph.D., A.I.C., and K. N. BAGCHI, B.Sc., M.B., F.I.C.

In a previous communication[1] we have shown that iodine can be determined colorimetrically by treating a solution of an iodide with acid permanganate and extracting the liberated iodine with carbon tetrachloride.

The method has been developed, and we have now succeeded in determining iodide colorimetrically in presence of fluorides, chlorides and bromides by oxidising an iodide solution with nitric acid before extracting the iodine with carbon tetrachloride. Maljaroff and Matskiewitsch[2] determine iodine by using nitrous acid and chloroform, but the iodine-chloroform extract obtained by their method remains turbid and does not become fit for colorimetric comparison for about an hour after the extraction is made, whereas the method described below gives quite a clear extract which can be matched immediately.

It has been found that acid permanganate (*N*/50 potassium permanganate with dilute sulphuric acid), which was successfully used in liberating iodine from a pure solution of an iodide, is not suitable for the determination of iodides when present with bromides. By using nitric acid of suitable strength, however, the iodides are selectively oxidised with liberation of iodine, whilst the other halides are not affected in any way.

The presence of other salts, such as the sulphates, phosphates or nitrates of sodium, potassium, calcium, magnesium, etc., either individually or in mixtures, does not interfere either with the extraction of iodine or with the production of the proper tint of the extract. If the concentration of the halides, especially that of magnesium iodide, does not exceed 1·5 per cent., the extraction and accurate determination of iodine can be carried out quite satisfactorily. No loss of iodine results from the presence of the salts contained in sea-water.

To obtain an accurate result the iodide solutions should be diluted to a concentration of about 0·01 per cent., so that a very small amount of the oxidising agent will liberate iodine without oxidising the bromides. If, on the other hand, a higher concentration of the iodide solution is employed for the determination, it will necessitate the use of a comparatively larger quantity of nitric acid, which is likely to decompose the bromides as well. The bromine so liberated will change the colour of the iodine solution and so render the test useless.

The reagents and apparatus required are as follows:—(1) Pure nitric acid (sp.gr. 1·4) diluted to about 5 *N*.[3] (2) Carbon tetrachloride (b.p. 76° C.). (3) Standard potassium iodide or sodium iodide solutions of concentrations varying from 0·0005 to 0·01 per cent., as required. (4) Separating funnel, 50 to 100 ml., with a short stem. (5) A colorimeter of the Duboscq type.

Procedure.—(*a*) *Preliminary Estimation.*—With the view of forming an idea of the depth of colour that will be produced by a definite volume of the unknown solution and the minimum amount of nitric acid required for complete oxidation, a preliminary test may be found useful. Five ml. of carbon tetrachloride and

10 ml. of the unknown solution are put into a test tube, and nitric acid is added, drop by drop, from a burette, until the resulting brown colour of the upper layer ceases to increase in intensity. When the test-tube is shaken, the carbon tetrachloride takes up the liberated iodine and becomes pink. The amount of nitric acid used is noted. It has been found that for 10 ml. of a 0·01 per cent. iodide solution about 2·5 to 3 ml. of nitric acid are sufficient to complete the oxidation. If it is seen that the tint thus obtained is too deep or too pale, the amount of the unknown solution taken should be decreased or increased accordingly. Tints either too deep or too pale are not suitable for comparison, because the smaller degrees of difference cannot be accurately judged. The depth of colour in this preliminary colour-test gives an idea of the concentration of the standards to be selected for the actual determination. The choice of the right depth of the tint is a matter of experience which is readily gained by a couple of determinations.

(*b*) *Actual Determination.*—About 5 ml. of carbon tetrachloride are placed in a separating funnel, and a definite volume of the unknown solution, an idea of the iodine-content of which has already been formed in (*a*), is introduced. Then about 2·5 ml. of nitric acid are slowly added from a burette directly into the solution and not down the sides of the vessel. The funnel is at once shaken vigorously, and the liberated iodine is taken up with carbon tetrachloride, leaving the upper layer colourless. The carbon tetrachloride extract is transferred to a graduated test-tube, about 4 ml. of carbon tetrachloride are added to the solution, and about 1 ml. is allowed to flow through the funnel (without shaking) into the test-tube to rinse out the stem. A few drops more of nitric acid are added to see whether more iodine is liberated. If so, it is again shaken out, and the extracts are united in the same test-tube. The volume is made up to 10 ml. with carbon tetrachloride, and the liquid is thoroughly mixed, then covered with a layer of water to prevent loss of carbon tetrachloride by evaporation, and set aside. A definite amount of each of the standard iodide solutions of two different concentrations—one of a higher and the other of a lower concentration than that of the unknown sample, as judged by the preliminary colour reaction—is placed in each of two separating funnels. Suitable strengths as standards for the comparison are 0·005 and 0·01 per cent. These standard solutions are then treated in exactly the same way as described above, and the carbon tetrachloride extracts are transferred to test-tubes and labelled. It is always desirable, but not essential, to take the same amount of the standard solutions as that of the unknown actually taken for the determination.

(*c*) *Colorimetric Comparison.*—One of the standard carbon tetrachloride extracts which seems to approximate closely to the unknown sample in depth of colour, is transferred from the test-tube to a matching cup, which is placed on the left-hand side of the colorimeter and set at 20 mm. The unknown extract is placed in another cup on the right-hand side, and the tints are matched in the usual way. The readings are noted, and the results are calculated in the usual way.

Table II gives the results of a few determinations of iodides in mixtures containing fluorides, chlorides, bromides and other salts, the composition of which is shown in Table I.

TABLE I

Composition of Mixtures of Halides taken for Determination

Other salts (sulphates, phosphates or nitrates of sodium, potassium, calcium and magnesium) were also added in various proportions to give a total volume of 100 ml.

	0·1 per cent. solution of potassium iodide or sodium iodide ml.	1·0 per cent. solution of sodium fluoride ml.	1·0 per cent. solution of sodium chloride ml.	1·0 per cent. solution of potassium bromide ml.
No. 1 mixture containing	8·8(KI)	10·0	20·0	15·0
No. 2 ,, ,,	12·6 ,,	10·0	25·0	20·0
No. 3 ,, ,,	15·8 ,,	15·0	30·0	20·0
No. 4 ,, ,,	3·0 ,,	20·0	10·0	10·0
No. 5 ,, ,,	12·0 ,,	15·0	10·0	5·0
No. 6 ,, ,,	25·5 ,,	15·0	10·0	10·0
No. 7 ,, ,,	19·5(NaI)	20·0	10·0	20·0
No. 8 ,, ,,	4·4 ,,	20·0	15·0	25·0
No. 9 ,, ,,	11·0 ,,	25·0	10·0	30·0
No. 10 ,, ,,	0·5 ,,	30·0	10·0	20·0

TABLE II

Results showing the Percentage of Iodides found in the Mixtures given in Table I

No.	Colorimeter reading of the unknown. Standard set at 20 mm.	Concentration of the standard Per Cent.	Amount found Per Cent.	Amount taken Per Cent.	Difference Per Cent.	Remarks
1.	22·6	0·01	0·00885	0·00880	0·00005	
2.	15·8	0·01	0·001265	0·00126	0·000005	
3.	12·5	0·01	0·0160	0·0158	0·0002	
4.	34·0	0·005	0·0030	0·0030	Nil	
5.	16·5	0·001	0·00121	0·00120	0·00001	
6.	15·5	0·01	0·0258	0·0255	0·0003	
7.	10·2	0·01	0·0196	0·0195	0·0001	
8.	34·0	0·005	0·00441	0·00440	0·00001	Standard set at 30.
9.	18·2	0·01	0·01099	0·0110	0·00001	
10.	35·5	0·0005	0·000493	0·00050	0·000007	Standard set at 35. 40 ml. solutions taken.

Our thanks are due to the Director of Public Health, Bihar and Orissa, for affording various facilities for carrying out this investigation in the Public Health Laboratories.

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CHEMICAL LABORATORY
PUBLIC HEALTH DEPARTMENT
PATNA, INDIA

Electrometric Analysis of Ferrous Sulphate Solutions

By N. A. SHISHACOW

When compared with other methods of analysis of iron salts, electrometric titration has proved to be undoubtedly the best. It involves great difficulties, however, and I therefore thought it might be useful to investigate the properties of ferrous sulphate solutions themselves before I studied the action of *X*-rays upon them (*Phil. Mag.*, 1932, **14**, 198). As the results of these investigations have been described elsewhere (*J. of Gen. Chem., Russia*, 1931, **1**, 1012), I will only summarise them, and then draw some further conclusions from them.

Under the influence of atmospheric oxygen ferrous sulphate solutions are subject to spontaneous oxidation, and this process takes place more rapidly when the concentration of sulphate is high. In Table I is shown the percentage of the oxidation of pure sulphate solutions in 0·1 *M* sulphuric acid after a period of approximately 180 days.

Table I

Concentration Molar	Oxidation Per Cent.
0·001	2
0·01	8
0·98	28
0·107	45
0·45	72

Spontaneous oxidation takes place also in darkness, but at a slower rate. This oxidation proceeds with pronounced rapidity when platinum or platinum black is immersed in the solution (see Table II).

Table II

	4 Days Per Cent.	9 Days Per Cent.
0·1 molar without platinum	3	4
0·1 ,, with platinum	38	40
0·1 ,, ,, ,, black	85	100
0·001 ,, ,, ,, ,,	100	100

By taking into account the influence of the platinum, it is possible to develop a more perfect electrometric method. When a platinum electrode is being dipped into a solution containing ferrous sulphate an excess of ferric ions immediately begins to accumulate around it. To this is due the gradual increase in the oxidation-reduction potentials which always follows the use of a platinum electrode, and also an increase in the concentration of the ferric ions in solution.

It is obvious, therefore, that with a platinum electrode not the true potential, but a higher one, is being observed. The corresponding error depends on the period during which the platinum wire remains at the same place in the liquid; it will be smaller when this period is shorter, *i.e.* when the quantity of the ferric

ions surrounding the wire is also small. It is also obvious that when the renewal of the adjacent layer of the solution takes place more rapidly, the apparent potential of the solution will approach more nearly to the true one. Therefore, checking the bilogarithmic curve, I had to use a fast-moving platinum electrode (the speed of the rotation was 100 to 600 R.P.M.). In this way I succeeded in proving that the bilogarithmic equation

$$\epsilon = \epsilon_0 + 0{\cdot}058 \log. \frac{C_3}{C_2} \quad .. \quad .. \quad .. \quad (1)$$

is quite correct at concentrations of ferrous ions between 99·9* and 0·002 per cent., especially in the right part of the curve. This result is more accurate than those obtained by other chemists.†

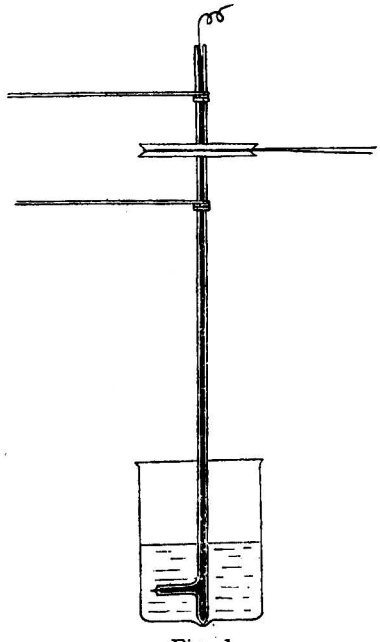

Fig. 1

In this way, by using a rotating platinum electrode (Fig. 1), it would be possible, by means of electrometric titration, to obtain results of a high degree of accuracy. Indeed, it may be possible to obtain very accurate data without titration, simply by measuring the oxidation-reduction potentials.

If the equation (1) is correct, it must be possible to determine the ferrous ion concentration C_2 (or ferric ions, *i.e.* $C_3 = 1 - C_2$) by the use of the inverse equation:

$$C_3 = \frac{10^{\frac{\epsilon-\epsilon_0}{b}}}{1 + 10^{\frac{\epsilon-\epsilon_0}{b}}}, \quad .. \quad .. \quad .. \quad .. \quad (2)$$

supposing b to equal 0·058; the value ϵ_0 may be found by interpolation; for instance, until the jump of the potential the course of the titration always remains independent of the concentration of sulphate, at least when the concentration ranges from 0·1 M to 0·001 M. (When the concentrations are lower the curves rise higher and the jump of the potential is less pronounced.) When, at a given concentration of the sulphate, the concentration of the sulphuric acid is increasing, the bilogarithmic curve is shifted downwards, parallel to itself. If we follow the course of this shifting at the middle point ϵ_0, which corresponds with the ratio of the concentrations $\frac{C_3}{C_2} = \frac{50 \text{ per cent.}}{50 \text{ per cent.}}$, the dependence of this E.M.F., ϵ_0, on the acid concentration may be represented by the curve (Fig. 2), where ϵ_0

* I could not approach nearer the 100 per cent. concentration of ferrous ions, owing to the rapid oxidation of pure ferrous solutions immediately after their preparation.

† For instance, see Peters, *Z. phys. Chem.*, 1898, **26**, 193. The data which he obtained are included in the Landolt-Börnstein Tables (1929), as well as in all the books edited by Foerster, *Electrochemie wässeriger Lösungen*, including that edited in 1923. See also Fricke and Morse, *Phil. Mag.*, 1929, **7**, 134.

is measured against a normal calomel electrode. If, when working with oxidation-reduction potentials, sufficiently strong sulphuric acid* is used (*e.g.* 0·1 to 1·0*M*), the constant ϵ_0 will be determined with reasonable accuracy.

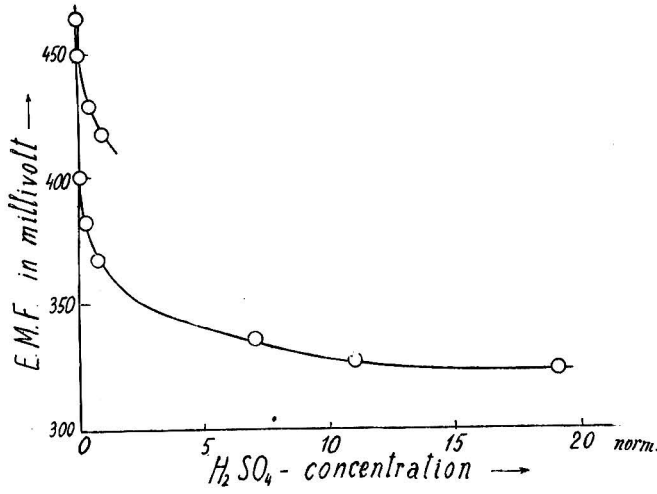

Fig. 2

As may be seen from Table III, the right-hand part of the bilogarithmic curve is very accurate. In the left-hand part, especially in the region of the more gradual course of the curve (40 per cent. to 80 per cent. Fe‴), the accuracy may be increased by adding a definite quantity of potassium dichromate. This quantity must be such as to raise the ferric ion concentration to the region of highest sensitivity of the curve, for instance, to 97 to 98 per cent. Fe‴. In this way, having two measurements of the oxidation-reduction potentials, the quantity of ferric ions present may be determined with an accuracy of about 0·1 to 0·2 per cent.† I should like to note also, that when, in accordance with modern theory, we substitute in the equation (I) for the concentration, the so-called "activities," *i.e.* if we write it in the form

$$\epsilon = \epsilon_0 + 0{\cdot}058 \log. \frac{C_3}{C_2} \cdot \frac{f_3}{f_2} \quad .. \quad .. \quad .. \quad (3)$$

and compute these coefficients of activities f_3 and f_2, making use of the Debye–Hückel formula, it will be seen that, in the case of a change in the ratio of concentration, the correcting term $0{\cdot}058 \log. \frac{f_3}{f_2}$ does not change much. It has an effect only on the constant ϵ_0; for practical purposes this is of no importance, so that the old equation (I) still remains valid.

* For electrometric titration more concentrated sulphuric acid is especially suitable, owing to its very pronounced jump (Hosteller and Roberts, *J. Amer. Chem. Soc.*, **1919**, **41**, 1345).

† If the total quantity of iron in the solution is unknown, it will be sufficient to determine it by the addition of a known quantity of potassium dichromate, so that the prior and subsequent oxidation-reduction potentials both remain on the sensitive part of the bilogarithmic curve.

TABLE III

0·42 *N* Sulphuric Acid; $\epsilon_0 = 0{\cdot}380$ Volt

Oxidation-reduction potential V	Ferric sulphate, calculated Per Cent.	Ferric sulphate, found Per Cent.
0·3047	4·79	4·88
0·3498	23·58	23·18
0·3727	42·80	42·08
0·3925	62·16	60·94
0·4160	80·68	80·06
0·4581	95·69	95·64
0·4631	96·45	96·24
0·4709	97·36	97·20
0·4852	98·49	98·38
0·4992	99·13	99·16
0·5213	99·79	99·74

It is thus seen that when a rapidly rotating platinum electrode is employed, the old bilogarithmic equation (I) is correct at concentrations of ferrous ions between 99·9 and 0·002 per cent. It is thus possible to obtain very accurate results without titration, simply by measuring the oxidation-reduction potentials. In such a way the percentage of ferric ions present may be determined with an accuracy of about 0·1 to 0·2 per cent. The total quantity of iron in the solution may be determined by adding a small quantity of potassium dichromate and measuring the oxidation-reduction potentials before and after the addition.

WOLCHOWSKOY, 3
LENINGRAD

Notes

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

A QUALITATIVE REACTION FOR THE DETECTION OF LIGNONE SULPHONATES (SULPHITE WASTE LIQUOR)

WASTE liquor from the manufacture of cellulose pulp by the sulphite process has come to be a constituent, legitimate or otherwise, of very varied commercial products. Either crude or after some simple "processing," it is found in such diverse materials as fireproof cements and tanning liquors. Its detection is sometimes important. A very easy and fairly sensitive qualitative test has been used in this laboratory for ten years, but only lately was the fact brought to my notice that, though the reaction involved has no novelty, its utility for the detection of the lignone sulphonates has not been elsewhere noted. It has here been found that a convenient *modus operandi* is as follows:—About 10 ml. of a filtered aqueous extract of the material under examination are warmed with 0·5 g. of potassium chlorate till the reagent is dissolved. The solution is cooled and cautiously

acidified with hydrochloric acid (sp.gr. 1·20), of which 10 ml. or more should ultimately be added. If a lignone sulphonate (the characteristic constituent of sulphite waste liquor) is present, a marked orange-red colour will develop on warming. If the amount present is great enough, an orange-red solid, which has a gummy consistence when hot, will separate as the reaction proceeds. At the same time there is usually a considerable evolution of gas. The red colour is easily distinguished from the yellow which would be produced by the mutual action of potassium chlorate and hydrochloric acid alone. The insoluble chlorine compound which is formed in the above reaction seems to be the same as that noted by Seidel and Hanak (*Mitteilung aus dem Technischen Gewerbe Museum*, Wien, 1897, **7**, 283; Abst. *J. Soc. Chem. Ind.*, 1898, **17**, 596), as well as by subsequent observers.

ALFRED TINGLE

CUSTOMS-EXCISE LABORATORY
OTTAWA, CANADA

SOME CHARACTERISTICS OF "LIMONITES" USED IN THE CURE AND PREVENTION OF BUSH SICKNESS

FOR the past three years Whangarei (Ruatangata) limonite, introduced by Aston as an economical cure for bush sickness in stock in the Rotorua district of New Zealand, has been used with unfailing success. For some reason, however, limonites from different deposits in New Zealand have been found to differ very markedly in their efficacy as a cure for bush sickness, and the present investigation was undertaken to correlate, if possible, the chemical properties of these limonites with the field tests.

Chemical analysis of the efficacious Ruatangata and Okaihau ores and the relatively ineffective Onekaka and Puhipuhi ores showed that, in addition to iron oxide (62·30–71·25 per cent.), silica and water, the following elements were present in small amounts in some or all of the ores:—Titanium, calcium, magnesium, manganese, phosphorus, sulphur, barium, sodium and potassium, together with traces of copper, chromium, arsenic, antimony, nickel and cobalt.

A further analysis of 21 samples, derived from four different deposits, showed that in most cases the commercial samples found by field trials to be ineffective in curing bush sickness were low in combined water and contained appreciable amounts of calcium carbonate. With one exception, the ores contained less than 1·0 per cent. of ferrous oxide.

Although solubility experiments with dilute hydrochloric or dilute oxalic acid solution showed no striking correlation with the field evidence, it was found that, in the presence of reducing agents, under certain conditions the effective limonites were from twice to four times as soluble as the ineffective samples. It was found with an acetic acid and sodium acetate solution (pH 4·0), in which the limonite samples are insoluble, that the amount of iron dissolved at equilibrium was directly proportional to the amount of sodium hydrosulphite added (as reducing agent) and practically independent of the nature of the limonite. It was shown, however, that the rate of solution of the iron in the acetic acid and sodium acetate buffer solution (pH 4·0) containing 1·25 per cent. of sodium hydrosulphite was much greater with the effective samples—a fact suggesting that the curative value of the ores was to be correlated with the rate of solution of the iron in acid-reducing agents rather than with the total solubility of the iron at equilibrium.

As a general method of differentiation between limonite samples, a sugar hydrochloric acid reagent was used. This reagent was prepared by dissolving 100 g. of commercial sucrose in 1 l. of $N/10$ hydrochloric acid made up with freshly-boiled distilled water. In the solubility test 0·5 g. of limonite and 50 ml. of the reagent were placed in a 200-ml. conical flask, which was immediately stoppered with a tightly-fitting cork provided with a Bunsen valve to protect the solution

from oxidation by air. The flask was shaken in boiling water for 15 minutes, and the solution was then quickly cooled, made up to 100 ml. with water, and immediately filtered through a No. 42 Whatman paper. After approximately 20 ml. of the filtrate had been collected, the funnels and filter papers were removed to exclude the possibility of further solution of the limonite, and a suitable aliquot portion was taken for the determination of the iron.

Heating tests showed no striking change of solubility in sugar hydrochloric acid unless the sample had been heated above 550° C. Fineness of grinding, as determined by sieving tests, was not found to have any appreciable effect upon the solubility of the ore in the sugar hydrochloric acid reagent.

R. E. R. GRIMMETT
F. B. SHORLAND

DEPARTMENT OF AGRICULTURE
WELLINGTON, NEW ZEALAND

THE ACIDS OF CIDER

THE barium salts of tannic and citric acids are practically insoluble in 20 per cent. (by vol.) alcohol; those of malic and succinic acids are soluble in 20 per cent. alcohol, but insoluble in 75 per cent. alcohol; and the barium salts of lactic and acetic acids are soluble in 75 per cent. alcohol.

Malic acid is the chief acid of apple juice; it is fermented to lactic acid. According to the equation for this fermentation 134 parts of malic acid (= 150 of tartaric acidity) give 90 parts of lactic acid (= 75 of tartaric acidity). Citric acid is said to be present in apple juice, but my tests have given negative results. Succinic acid, a metabolic product of yeast, is present in all fermented drinks, forming about 0·5 per cent. of the sugar fermented; the quantity in cider will therefore be small. Acetic acid is formed by acetification of alcohol.

The fermentation of the malic acid follows the primary alcoholic fermentation, and is most noticeable in sharp highly nitrogenous juices. These undergo a very rapid alcoholic fermentation and soon go dry; then in quite a short time the original acidity may have been more than halved. In order to prevent cider sickness, it is inadvisable at any time to let the acidity of the cider sink below 0·5 to 0·55 per cent. (as tartaric acid). Hence, it is often necessary to make a small addition of acid even to pure juice. Tartaric, citric, lactic, and even acetic acid have been used, the price of malic acid, so far, being prohibitive. If such juices are diluted to moderate the rate and extent of the alcoholic fermentation, the need for an addition of acid will be obvious.

The following figures indicate the nature of the changes taking place in samples of apple juice fermented in the laboratory at room temperature.

Weeks	Acidity Per Cent.	Malic acid (as tartaric acid) Per Cent.	Lactic acid Per Cent.	Acetic acid Per Cent.
0	1·23	1·03	(0·23)	—
2	1·14	0·79	0·09	0·04
6	0·86	0·48	0·35	0·05
10	0·81	0·37	0·41	0·14
0	1·11	0·96	(0·15)	—
2	0·95	0·69	0·18	0·01
6	0·53	0·14	0·54	0·04
*10	0·54	0·09	0·60	0·06
0	0·92	0·71	(0·24)	—
4	0·46	0·12	0·53	0·04
10	0·50	0·13	0·53	0·09

* The same juice hydrolysed gave: malic acid, 0·09; lactic acid, 0·76; and acetic acid, 0·06 per cent.

A small amount of "malic" acid persists even in cider vinegar, whilst lactic acid diminishes as cider ages. Titration of an old sample of cider vinegar gave 5·03 per cent. of acidity (as acetic acid), and the vinegar contained 5·04 per cent. of acetic, 0·18 per cent. of lactic, and 0·08 per cent. of malic acid.

In sub-acid and slow-fermenting juices the alcoholic and malic fermentations occur simultaneously, and such juices may even show lactic acid production from sugar. In a cider cellar the above changes take place more slowly, owing to the lower temperature, and they can be moderated by various means. The following are figures for typical examples of commercial ciders:

Grade	Acidity Per Cent.	Malic acid (as tartaric acid) Per Cent.	Lactic acid Per Cent.	Acetic acid Per Cent.
A (P.J.)	0·64	0·20	0·26	0·30
B (P.J.)	0·63	0·15	0·43	0·22
C (N.M.)	0·50	0·13	0·36	0·10
D (N.M.)	0·57	0·13	0·45	0·08
E (D.)	0·62	0·13	0·17	0·11

None of these samples contained added acid except sample E, a draught cider with 0·29 per cent. of tartaric acid. (The 20 per cent. alcohol cannot quite be relied on to exclude tartrate.)

I. *Acetic Acid.*—One hundred ml. of cider are heated to incipient boiling and then transferred to a steamed-out distilling flask, 100 ml. of water, containing 3 ml. of *N* sulphuric acid are added, 100 ml. are distilled, and the distillate is titrated with *N*/10 sodium hydroxide solution, phenolphthalein being used as indicator. Of the acetic acid present, 36·6 per cent. distils.

II. *Lactic and Acetic Acids.*—Twenty ml. of the cider are neutralised with a saturated solution of barium hydroxide in a 110-ml. measuring flask (phenolphthalein as indicator). Two ml. of 10 per cent. barium chloride solution and about 81·5 ml. of industrial methylated spirit (74 O.P.) are added, and the liquid is cooled, again neutralised, and made up to 110 ml. with water. After standing for 3 hours at 15 to 18° C., it is filtered through a dry filter. (Any excess of barium hydroxide should be precipitated by means of a current of carbon dioxide and the liquid re-filtered.) From 75 ml. of the filtrate most of the alcohol is evaporated, 2 ml. of a 10 per cent. solution of anhydrous sodium sulphate are added, and the residue is dried and ignited. It is then warmed for 5 minutes on the water-bath with 20 ml. of *N*/10 hydrochloric acid in a covered vessel, and titrated back with *N*/10 sodium hydroxide solution. $(\text{Ml.} \times \frac{110}{75} \times 5)$ gives the lactic and acetic acid per 100 ml. of cider in terms of *N*/10, and the acetic acid equivalent is subtracted to obtain the lactic acid.

III. *Malic, Lactic and Acetic Acids.*—Fifty ml. of cider are neutralised with barium hydroxide solution in a 100-ml. measuring flask, and then treated with 5 ml. of barium chloride solution and 20 ml. of alcohol (74 O.P. spirit), diluted, cooled, and made up to 100 ml. after being again neutralised. The mixture is allowed to stand for 3 hours, and then filtered, and 25 ml. of the filtrate are treated as described above. (Ml. × 4 × 2) gives the equivalent of the acetic, lactic and malic acids. The malic acid is obtained by difference. The operations are carried out at 15° to 18° C.

If in (II) the total acidity (as tartaric acid) in the cider exceeds about 0·8 per cent., less than 20 ml. of the cider must be taken.

In (III) the actual percentage of malic acid in the cider must not exceed 0·5, 0·4 and 0·3 per cent. if the alcohol-content of the cider is 0, 5 and 10 per cent., respectively; otherwise less than 50 ml. must be taken.

On the Continent a similar test is used for lactic acid in wine, but is not considered accurate if the sugar-content exceeds 0·5 per cent. Sugar does appear

to increase the apparent lactic acid figure a little; hence, so far as possible, my results have been obtained with dry samples.

The following results were obtained with experimental mixtures:

Taken	Per Cent.	Found	Per Cent.
Sucrose	2·0		
Invert sugar	8·0		
Malic acid	0·2	Malic acid	0·19
Lactic acid	0·35	Lactic acid	0·37
		At 25° C.	
Tannin	0·15		
Malic acid	0·19	Malic acid	0·14
Lactic acid	0·40	Lactic acid	0·45
		At 20° C.	
Tannin	0·15		
Malic acid	0·19	Malic acid	0·20
Lactic acid	0·43	Lactic acid	0·44

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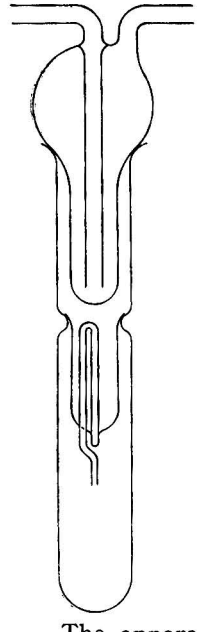
D. W. Steuart

The Laboratory
Wm. Gaymer & Son, Ltd.
Attleborough

A MICRO-EXTRACTION APPARATUS

The body of the apparatus is a tube, 6 in. long and 1 in. in diameter, the top being either flanged, or flanged and ground, to take a pear-bulb condenser, and the bottom closed as in a boiling tube. The actual extractor consists of a cup, 1½ in. long and ⅝ in. wide, with a syphon tube attached to the bottom and a flanged top to support it on three projections about 3½ in. from the bottom of the outside tube. The internal diameter of the syphon tube must be not less than 2 mm., or capillary attraction will cause it to syphon continuously. The pear-bulb condenser rests on the flanged top of the outside tube and extends down to within about ½ in. of the top of the extractor cup. When the apparatus is heated over a water-bath steam is apt to condense on the outside of the condenser and run into the apparatus. This can be prevented either by fitting the condenser with a ground-glass joint through the centre of which is a central vent, or by taking steps to keep the steam away from the apparatus. The latter method is recommended, as it obviates unnecessary complication of the apparatus and is quite easily and effectively carried out by keeping the bath covered and preventing the steam from escaping from between the inner ring and the apparatus by means of a disc of cardboard, or, better still, of metal, with a centre hole cut to fit the apparatus closely.



The method of heating is immaterial, but whatever method is employed, it is wise to have at least the outer tube constructed of resistance glass, such as Pyrex.

The apparatus holds about 10 ml. of solvent, and when the extraction is complete, the cup can be lifted out by the syphon tube with a thin wire hook and the solution can then be poured out easily without the slightest loss. There is a

Whatman's extraction thimble, 10 × 50 mm., which is of a convenient diameter for use in this apparatus, but is slightly too long. This can be cut down to the required length.

The volatile solvents in general use for hot extraction in the Soxhlet apparatus have been tested and found to work satisfactorily. With chloroform the apparatus syphons about 20 to 25 times an hour, and with ether slightly faster. Extraction is rapid, as it takes place at the b.p. of the solvent. One hour's extraction of phenacetin and caffeine tablets with chloroform gave a result only 0·05 per cent. below that obtained by three hours' extraction in the same apparatus, and these times compare very favourably with those taken by a larger extractor.

The apparatus will be found particularly useful in the analysis of tablets and pills from which it is necessary to remove the excipient, for the determination of non-volatile resins, etc., in vegetable tissue, and for the usual fat-extractions, and it has the advantages of being small, easily cleaned and requiring only small amounts of sample and solvent. It has been found that gentle and even boiling can best be obtained by putting a small glass bead into the outer tube with the solvent.

Arrangements have been made for this extractor to be obtained from Messrs. Baird & Tatlock, Ltd., at the price of 8s. 6d.

I wish to thank Mr. G. S. Stevens for his co-operation.

E. B. COLEGRAVE

DEPARTMENT OF CHEMISTRY
CHELSEA POLYTECHNIC
LONDON, S.W.3

A RAPID MICRO-BROMIDE TEST FOR THE DETECTION OF LINSEED OIL IN MUSTARD SEED OIL

THE insoluble bromide test, originally devised by Hehner and Mitchell (ANALYST, 1898, **23**, 310), has been used in most of the Public Health Laboratories in Bengal in the analysis of mustard-seed oil under the Bengal Food Adulteration Act. Mustard-seed oil, which is extensively consumed as an edible oil throughout India, particularly in Bengal, is frequently adulterated with linseed oil. Toms (ANALYST, 1928, **53**, 71) has devised a rapid micro-gravimetric method of determining the halogen absorption of oils and fats by exposing a film of the oil, derived from a single drop, on a weighed microscope slide in an atmosphere of bromine. While studying this "bromine vapour" method, it occurred to me that possibly a rapid qualitative test for the detection of linseed and other highly unsaturated fatty oils might be based on the behaviour of the brominated film when treated with ether and petroleum spirit (in which the mixed bromo-glyceride is almost insoluble), and experiments in this direction have given promising results. Considerable information may be gained at the outset by an examination of the physical condition of the brominated film, as was first suggested by Toms (*loc. cit.*). Thus, linseed oil and its distinctive fatty acids (linolenic acids) yield hard, colourless gritty films with wrinkled surface, whereas mustard-seed oil gives a soft, opaque and glossy film, without any tendency to wrinkle.

One drop of the oil (0·04 to 0·06 g.) is spread on a microscope slide (which must be free from grease) in a uniform film by drawing the narrow edge of a second microscope slide slowly along the whole length of the first slide at an angle of 30°. The slide is then exposed to an atmosphere of bromine for 20 to 25 minutes, after which it is left in the air for a short time to remove the excess of bromine.

After the physical appearance of the brominated film has been noted, the slide is placed horizontally on the edge of a small rectangular glass trough and covered with a mixture in equal parts of ether and petroleum spirit. The film is then stirred with a very thin glass rod and examined for the appearance of any

white, curdy precipitate, the whole of the slide being meanwhile kept covered with the mixed solvents. From the amount of flocculent precipitate (dilinolenic-linolic bromo-glyceride) an estimate may be formed of the quantity of linseed oil (or other oil yielding insoluble bromides) in the sample.

Ten samples of mustard-seed oil, tested in this way, gave no indications of a white, curdy precipitate; cotton-seed, arachis, kapok, and mowrah oils also gave negative results.

Abundant precipitates were obtained with linseed oils, boiled linseed oil, double-boiled linseed oil and fish oil. Mixtures of linseed oil with 5 to 50 per cent. of mustard-seed oil gave precipitates, the amounts of which were approximately proportional to the quantity of linseed oil present.

A mixture of 90 per cent. of cotton-seed oil with 10 per cent. of linseed oil showed a perceptible precipitate, but 2 per cent. of linseed oil could not be detected. Mustard-seed oil adulterated with 5 per cent. of linseed oil showed a considerable amount of precipitate, and with a 50 per cent. mixture the whole of the precipitate was practically insoluble in the mixed solvents.

Work is in progress with the object of making the test more strictly quantitative.

I wish to thank Rai J. N. Ghosh Bahadur, Chairman, District Board, Khulna, for facilities for working in the Board's laboratory, and Dr. M. M. Bose, Public Analyst and District Health Officer, for his keen interest and valuable suggestions throughout the work.

S. NEOGI

PUBLIC HEALTH LABORATORY
KHULNA, BENGAL

THE EFFECT OF VARYING STORAGE CONDITIONS ON THE DETERIORATION OF ERGOSTEROL

IT is well known that ergosterol is liable to deteriorate on storage. Mention of this was made by Bacharach, Smith and Stevenson (ANALYST, 1933, **58**, 128), but the only quantitative work bearing on this subject, so far as we are aware, is that done by Callow (*Biochem. J.*, 1931, **25**, 79), who reported the rate of gain in weight when ergosterol was stored in air over a dehydrating agent.

We have found it necessary, in connection with the large-scale manufacture of this material, to determine the change in specific rotation and m.p. during storage, and the results of our tests are given here.

Except where otherwise stated, each determination of the specific rotation was carried out as follows:—A 2 per cent. w/v solution of ergosterol was made, without the application of heat, in chloroform answering the requirements of the B.P., 1932. The rotation was observed in a 100-mm. or 200-mm. jacketed tube at 20° C. with sodium light. The specific rotation was calculated from the mean of about 10 readings made from 10 to 20 minutes after complete solution had been effected. The maximum variation from the mean reading was 0·02°, so that the error in the specific rotation recorded is less than 1·0 (100-mm. tube) or less than 0·5 (200-mm. tube).

In the determination of the m.p. the procedure of the B.P., 1932, was followed, the actual m.p. being the final temperature recorded.

Preliminary Experiments.—Prior to carrying out the keeping tests it was thought desirable to discover the effects produced on the optical rotation by varying the general procedure, outlined above, for preparing the solution, the length of time the solution was allowed to stand prior to examination, the type of chloroform used, the concentration, and the temperature at which the rotation was determined. These results are given in Table I.

TABLE I

	Sample	Specific rotation $[\alpha]_D$		Remarks
1. Effect of heat during preparation of solution.	A.	−122·3°	(100 mm.)	average of 6 determinations.
		−115·0	(100 mm.)	heated almost to b.p.
		−116·5	(100 mm.)	,, ,, ,, ,,
	B.	−126·4	(100 mm.)	average of 4 determinations.
		−121·0	(100 mm.)	heated almost to b.p.
	C.	−129·1	(100 mm.)	average of 5 determinations.
		−129·4	(100 mm.)	heated to 50° C. for 5 minutes.
2. Effect of standing in solution.	C.	−129·1		See above.
		−127·8	(100 mm.)	5 hours at lab. temp. in clear glass bottle.
		−114·9	(100 mm.)	24 hours at lab. temp. in clear glass bottle.
	D.	−128·5	(100 mm.)	
		−113·0	(100 mm.)	24 hours at lab. temp. in clear glass bottle.
	B.	−126·4		See above.
		−103·0	(100 mm.)	48 hours at lab. temp. in clear glass bottle.
3. Effect of concentration.	A.	−122·3		See above.
		−122·0	(100 mm.)	1 per cent. w/v solution.
4. Effect of temperature.*	E.	−118·5	(100 mm.)	old solution $t=16°$ C.
		−117·0	(100 mm.)	,, ,, $t=20°$ C.
		−114·0	(100 mm.)	,, ,, $t=25°$ C.
		−111·0	(100 mm.)	,, ,, $t=31°$ C.
		−109·0	(100 mm.)	,, ,, $t=37°$ C.
Effect of solvent and temperature.*	F.	−131·3	(200 mm.)	B.P. $CHCl_3$ $t=15°$ C.
		−129·8	(200 mm.)	B.P. $CHCl_3$ $t=20°$ C.
		−127·0	(200 mm.)	B.P. $CHCl_3$ $t=25°$ C.
		−131·7	(200 mm.)	Freshly distilled alcohol-free $CHCl_3$ $t=15°$ C.
		−130·0	(200 mm.)	,, ,, $t=20°$ C.
		−127·5	(200 mm.)	,, ,, $t=25°$ C.
		−126·5	(200 mm.)	alcohol-free $CHCl_3$ 4 days old (contains phosgene) $t=15°$ C.
		−124·2	(200 mm.)	,, ,, $t=20°$ C.
		−120·0	(200 mm.)	,, ,, $t=25°$ C.

* Uncorrected for expansion of solvent. This would account for a fall in specific rotation, for values between −110° and −130°, of 0·7° to 0·8° per 5° C. rise in temperature.

It was proved, therefore, that heating during the preparation of the solution and standing in solution should be avoided; that the temperature must be carefully controlled; that slight variations in the concentration have no appreciable effect; and that chloroform B.P. is preferable to "purified" chloroform, for the small amount of alcohol it contains has a negligible effect on the rotation, but prevents the production of abnormally low results caused by a partly-decomposed solvent.

Keeping Tests.—Optical determinations on stored samples were all carried out as described under the general procedure above, the 200-mm. tube being used. The material was stored either in amber glass bottles in the dark (marked "dark" in Table) or in clear glass bottles in diffused daylight (marked "light" in Table).

In the tests in which an atmosphere of nitrogen was used, the ergosterol was stored in 2-oz. bottles fitted with a rubber bung through which passed a glass tube reaching to the bottom of the bottle. The stopper being slightly loosened, nitrogen was passed into the bottle through the glass tube for several minutes and the bottle gently shaken. The rubber bung was then tightly secured, the supply of nitrogen stopped, and the entrance-tube closed. The nitrogen used was commercial cylinder-nitrogen containing less than 1 per cent. of oxygen.

The results are given in Table II.

In view of the figures of Tanret (*vide* Callow), Callow (*loc. cit.*), and Bacharach, Smith and Stevenson (*loc. cit.*), samples C, H, and J may be considered normal samples of commercial ergosterol of good quality. G is somewhat inferior.

TABLE II

Sample	Conditions of storage: Container, etc.	Atmosphere	Temperature	Period	Specific rotation $[\alpha]_D$	Melting-point °C.	Colour
C.		See Table I			−129·5°	162·8–163·2	
	dark	air	38° C.	7 weeks	−127·7		
	dark	nitrogen	38° C.	7 weeks	−129·6		
	light	air	lab.	7 weeks	−127·2		
	light	nitrogen	lab.	7 weeks	−128·5		
	dark	air	lab.	7 weeks	−128·5		
	dark	nitrogen	lab.	7 weeks	−130·0		
	dark	air	5° C.	7 weeks	−128·3		
	dark	nitrogen	5° C.	7 weeks	−130·2		
J.					−127·7		
	dark	air	lab.	17 weeks	−125·5		
C.	dark	air	38° C.	22 weeks	−105·5	141·5–145·0	strong yellow
	dark	nitrogen	38° C.	22 weeks	−113·7	146·0–151·0	pale yellow
	light	air	lab.	22 weeks	−126·5	159·2–160·0	slight yellow
	light	nitrogen	lab.	22 weeks	−126·0	159·5–160·2	slight yellow
	dark	air	lab.	22 weeks	−126·5	160·5–160·8	slight yellow
	dark	nitrogen	lab.	22 weeks	−127·2	160·7–161·2	slight yellow
	dark	air	5° C.	22 weeks	−126·2	161·6–162·1	pract. white
	dark	nitrogen	5° C.	22 weeks	−127·0	162·0–162·4	pract. white
H.					−128·2		
	dark	air	lab.	36 weeks	−124·5		
C.	dark	air	38° C.	52 weeks	− 65·2	133 –138	strong orange
	dark	nitrogen	38° C.	52 weeks	− 97·0	138 –148	strong orange
	light	air	lab.	52 weeks	−111·0	145 –153	mod. yellow
	light	nitrogen	lab.	52 weeks	−102·2*	134 –147*	yellow*
	dark	air	lab.	52 weeks	−119·2	154·5–156·0	mod. yellow
	dark	nitrogen	lab.	52 weeks	−122·2	158·0–159·5	mod. yellow
	dark	air	5° C.	52 weeks	−125·0	161·3–162·1	slight yellow
	dark	nitrogen	5° C.	52 weeks	−126·4	161·3–162·3	very sl. yellow
G.					−122·5		
	dark	air	lab.	3 years	−108·2		

* Very small sample; consequently, large surface exposed.

The figures in Table II, expressed as fall in specific rotation in degrees per week and fall in melting-point in degrees per week under the various conditions, are given in Table III.

TABLE III

Conditions	7 weeks (spec. rotn.) $[\alpha]_D$	17 weeks (spec. rotn.) $[\alpha]_D$	22 weeks (spec. rotn.) $[\alpha]_D$	22 weeks m.p. °C.	36 weeks (spec. rotn.) $[\alpha]_D$	52 weeks (spec. rotn.) $[\alpha]_D$	52 weeks m.p. °C.	3 years (spec. rotn.) $[\alpha]_D$	Sample
Dark, air, 38° C.	0·26	—	1·09	0·83	—	1·23	0·48	—	C.
Dark, nitrogen, 38° C.	0·01 gain‡	—	0·72	0·56	—	0·63	0·29	—	C.
Light, air, lab.*	0·33	—	0·14	0·15	—	0·35	0·20	—	C.
Light, nitrogen, lab.*	0·14	—	0·16	0·13	—	0·52†	0·31†	—	C.
Dark, air, lab.*	0·14	—	0·14	0·11	—	0·20	0·14	—	C.
Dark, air, lab.*	—	0·13	—	—	0·10	—	—	0·09	G.H.J.
Dark, nitrogen, lab.*	0·07 gain‡	—	0·10	0·09	—	0·14	0·07	—	C.
Dark, air, 5° C.	0·17	—	0·15	0·05	—	0·09	0·02	—	C.
Dark, nitrogen, 5° C.	0·10 gain‡	—	0·11	0·04	—	0·06	0·02	—	C.

* The tests were begun in September, and consequently the test-periods up to 36 weeks had a temperature-range of about 15° to 20° C. For the 1-year and 3-year periods the upper temperature-limit was about 30° C.

† See above.

‡ Probably due to slight initial dehydration.

Thus the substitution of nitrogen for air, storage in the dark and low temperatures reduce the rate of, though they do not entirely prevent, deterioration. Under these conditions an increase in rate of deterioration does not apparently occur with longer standing. With change of temperature from 5° C. to 15° C. the effect is not very marked, but it is considerable with further rise of temperature.

Our main object in this work was a consideration of deterioration during bulk storage, *i.e.* with quantities of at least 5 kg., and not with small quantities which could readily be stored in sealed glass tubes. Deterioration under these latter conditions has been dealt with elsewhere (*cf.* Callow, *loc. cit.*).

L. R. ELLISON
G. F. HALL

ANALYTICAL LABORATORY
BOOTS PURE DRUG CO., LTD.
NOTTINGHAM

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.

WHEAT ACT, 1932. LIABILITY OF CERTAIN CONSIGNMENTS OF IMPORTED "MIDDLINGS" TO QUOTA PAYMENTS

R. AND W. PAUL, LIMITED *v.* WHEAT COMMISSION

ON January 18th the Court of Appeal (Master of the Rolls, Lords Justices Slesser and Romer) delivered judgment on the appeal by the defendants against the judgment of Mr. Justice Roche (*cf.* ANALYST, 1934, **59**, 406).

The learned Judge had held that:

(i) Bye-law No. 20 was *ultra vires* and therefore the jurisdiction of the Court was not ousted in favour of arbitration. The defendants claimed that the Act and Bye-laws thereunder made provision for the final determination by arbitration of disputes arising in such matters as might be specified in the bye-laws.

(ii) The thirteen consignments in question were not "flour" as defined in the Wheat Act, but were "wheat offals" as defined in the Wheat Act, and therefore exempt from quota payment, and the plaintiffs were entitled to recover the sum of £1,912 5s. 2d., which had been paid as quota payments, and to a declaration of non-liability for payment where such payments had not yet been made.

(iii) The plaintiffs could not recover the money paid on the first three consignments, as the action had not been brought within six months. The defence of the Public Authorities Protection Act was entitled to succeed.

The Wheat Commission appealed against the findings adverse to it, and the plaintiffs made a cross-appeal against that part of the judgment based upon the Public Authorities Protection Act. Sir William Jowitt, K.C., and Mr. H. Hull appeared for the Wheat Commission, and Sir Leslie Scott, K.C., and Mr. J. Whyatt for the plaintiffs.

The Master of the Rolls, giving judgment, said that, in his view, the jurisdiction of the Court was not excluded in favour of arbitration. The claim of the plaintiffs appeared to lie outside the ambit of any arbitration required by the Wheat Act, 1932. As regards the proper construction to be placed upon the Wheat Act and the result of the sections and definitions and rules derived therefrom, he said: "A

miller or importer cannot escape the liability to quota payments by treating or using the resultant product of milling as offals, however small may be the amount of flour extracted from the wheat milled. The purpose of milling is to produce flour, not offals. Offals are residual products, and unless the products contain not more than 7½ per cent. of the parcel in the form of flour or other non-residual, the product is or is to be deemed flour. It is argued that under the definition of wheat offal, if the residual product, after some flour has been extracted, is intended for animal or poultry food, then although this residual may be rich in flour, it is none the less offal, and the liability to make quota payments does not attach to it. I cannot agree to this." He further indicated that his own construction of the Act led to a different conclusion from that of Mr. Justice Roche in the Court below, and it required an examination of the parcels to be made so as to determine whether they were within the latitude and consequent exemption allowed to offals. In respect of the liability of the consignments in question he said: "From the evidence as a whole I am satisfied that all these consignments were produced by stopping the milling of flour before it had passed to its normal conclusion. They are not offals or residual products extracted in the process of milling wheat. With great respect to the learned Judge, I have come to the conclusion that all these parcels are subject to the quota payments, with the result that on this point the judgment must be reversed, and the plaintiffs' claim for repayment of the £1,912 5s. 2d. dismissed with costs."

Upon the cross-appeal the Judge was right in holding that the Public Authorities Protection Act applied to protect the defendants. The cross-appeal must be dismissed with costs.

Lord Justice Slesser read a judgment agreeing that the appeal should be allowed and the cross-appeal dismissed.

Lord Justice Romer, in the course of his judgment, said: "The plaintiffs have failed to show that any of the consignments in question can properly be described as wheat offals and their action should have been dismissed." In his opinion the appeal must be allowed and the cross-appeal dismissed.

The appeal was allowed with costs, and the cross-appeal dismissed with costs.

Leave to appeal to the House of Lords was given.

SALE OF DRIED ALFALFA AS TEA*

In this case the United States Attorney of the Northern District of Illinois, acting upon a report by the Secretary of Agriculture, asked for seizure and condemnation of 51 packages of dried alfalfa at Chicago, Ill., alleging that the article had been shipped in inter-state commerce from California, and charging adulteration and misbranding in violation of the Food and Drugs Act. The article was labelled "——American Vegetable Tea Orange Pekoe Type Green."

Analysis of a sample by the U.S.A. Department of Agriculture showed that it consisted of dried alfalfa. It was alleged in the charge that the article was adulterated in that dried alfalfa had been substituted for tea of the Orange Pekoe type, which the article, by reason of the labelling, purported to be.

Misbranding was also alleged under the provisions of the Act relating to drugs, in that the labelling of the article bore unwarranted curative and therapeutic claims, as "a tonic in nutritional and secondary anaemia, general blood impoverishment, dietary deficiencies, malnutrition and gastro-intestinal disturbances, and debilitated states," etc.

On June 15th, 1933, no claimant having appeared for the property, judgment of condemnation and forfeiture was entered, and it was ordered by the Court that the product be destroyed by the United States Marshal.

* U.S.A. Dept. of Agriculture. Food and Drug Administration. Notices of Judgment under the Food and Drugs Act. No. 21199. Issued August, 1934.

EFFECTS OF TRICHLOROETHYLENE

AN inquest was held on January 6th at Birmingham on the body of a man who had died suddenly on December 8th. He had been employed by a firm at Smethwick in degreasing plated cycle handlebars by means of trichloroethylene contained in a machine of special construction which had been in use since 1932. The solvent in the iron tank of this machine was converted into a heavy vapour, which condensed upon the handle bars placed inside and freed them from grease.

The works manager said that men on night duty were allowed to smoke while at work, and he had not been aware that Imperial Chemical Industries, Ltd., had issued regulations in which there was a warning against smoking when working with a degreasing machine in which trichloroethylene was used. He had since been informed that if the vapour were inhaled through a cigarette, there was a possibility of its being converted into phosgene.

Mr. B. P. Crawshaw, who designed the machine in question, said that there had been four deaths in Germany, from trichloroethylene poisoning, but not in connection with a degreasing plant. In his opinion it was perfectly safe to use the machine, and there were a large number of them working in this country.

Dr. J. C. Bridge, Senior Medical Inspector of Factories to the Home Office, said that there had been four or five deaths in England through using trichloroethylene, and information on the subject had been published in the Chief Inspector's Annual Report (*cf.* ANALYST, 1934, **59**, 626).

Mr. H. Shaw, an industrial chemist, Imperial Chemical Industries, Ltd., said that trichloroethylene had been in use for degreasing for about ten years. It could have acute effects if taken in quantity, but there was no evidence that small doses could poison a man. Two years ago Imperial Chemical Industries, Ltd., having made tests, warned the owners of degreasing plants not to allow smoking. If air containing 0·1 per cent. of trichloroethylene vapour were drawn through a cigarette, the temperature of the lighted end being about 600° C., the air inhaled would contain about 3 parts per million of phosgene. In reply to a question as to what was a fatal dose of phosgene, Mr. Shaw said that he thought that it was 25 parts per million. Rats subjected to trichloroethylene vapour over a period of six months had shown no signs of poisoning; in fact, they had increased in weight.

Dr. Whitelaw, pathologist, said that he could discover no natural cause of death.

Professor Haswell Wilson, of Birmingham University, said that there was no evidence of gaseous poisoning, but that there was paralysis of the respiratory centre. He could find no evidence that death was due to a natural cause, but attributed it to paralysis of the respiratory centre caused by some poisonous substance. Trichloroethylene poisoning by inhalation could be excluded, and there was no evidence of acute or chronic phosgene poisoning.

The jury found that death was due to natural causes.

Agricultural Research Council

REPORT FOR THE PERIOD, JULY, 1931, TO SEPTEMBER 30TH, 1933*

THIS Report, covering the first two years of the Council's existence, gives a survey of the state of agricultural science in Great Britain in the years 1931 to 1933, and also describes the activities of the Council, with its Committees and Sub-Committees, during that period.

After a preliminary introduction, outlining the functions of the Council and its relations with the Medical Research Council and the Department of Scientific and Industrial Research on the one hand, and, on the other, with the Agricultural Departments and the Development Commission, the Report describes its procedure, and the nature of the subjects assigned to its six Standing Committees.

Part II (pp. 13–20), dealing with the Economic Outlook, discusses *inter alia* the policy of "controlled industry," and the application of economic principles, including the theory of prices, to agricultural practice.

Part III, on SOIL (pp. 21–43), opens with an introduction on the nature of soil, and this is followed by a section on Soil Physics, in which an outline is given of the physical work carried out at Rothamsted from 1913 to the present time.

The "sticky point value," suggested by F. Hardy, has been subjected to critical examination by Keen and others, and it has been shown that the percentage of moisture in a thoroughly kneaded mass of soil which is just sufficiently moist to stick to the fingers or a knife is related, in the case of calcium clay soils, to the colloidal complex of the soil.

A second promising method, recently devised at Rothamsted by Schofield and Scott Blair, aims at ascertaining the "heaviness" of a soil in the agricultural sense; and in normal soils, where heaviness is correlated with clay-content, it indicates the amount of clay present. The method consists in ascertaining the weight which must be applied to a thin cylinder of moist soil in order to cause elongation; the test is made in a specially designed machine termed a pachimeter.

Soil Biology.—An outline is given of the work done by three Departments at Rothamsted since 1908. It has recently been shown by Cutler that there are organisms quite distinct from those described by Winogradsky, which share in the formation of nitrates.

SOIL CHEMISTRY.—Although no sharp distinction can be made, broadly it would be true to say that, whilst the Rothamsted studies aim at relating soil to plant-growth, the Scottish and Welsh investigators have had as their main purpose the study of the soil itself. As one result of these studies it may be claimed that it is now possible to begin the work of classifying British soils on a satisfactory basis.

With regard to soil reaction it is pointed out that, whilst the *p*H value has been shown to be a very useful figure for comparing the lime status of soils of similar origin, and the requirements of crops growing in similar climates, it does not follow that a series of *p*H values compiled to show the relative tolerance of crops to acidity in, *e.g.* the English Midlands, would hold good for soils in north-east Scotland.

Advances in the theories of soil reaction and base exchange have thrown new light on changes occurring in experimental plots at Rothamsted. Superphosphate was long suspected of increasing soil acidity, but the history of the Woburn plots has proved the suspicion to be unfounded. Long-continued applications of

* Report to the Committee of the Privy Council for the Organisation and Development of Agricultural Research, 1934, pp. 205. Cmd. 4718. To be purchased from H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 3s. net.

superphosphate to this soil, naturally deficient in lime, have not reduced the quantity of exchangeable bases. At Rothamsted, again, base-exchange theory provided Page with an explanation of the very serious damage suffered by clay soils when flooded by sea-water.

The relative proportions of silica to alumina, and of silica to alumina and ferric oxide, in the different soil horizons, depend both on the parent material and upon the degree of weathering; hence, climate has been adopted in many countries as the chief factor in classifying soils. In the cool humid climates of Northern Europe the molecular SiO_2/Al_2O_3 ratio may be 3 : 1 in the upper soil horizons; in the lower, ratios of 2 : 1 might be expected. In arid countries ratios of 5 or 6 : 1 may be found, and in the humid tropics ratios of less than 2 : 1 are common. The conclusions of Robinson on the ratios of Welsh soils, and those of Crowther on American soil ratios are discussed in the report.

Reference is made to the mineralogical analyses of soils by Hendrick and Newlands and by Hart. Even from the small number of soils (60 to 70) hitherto reported on, it may be inferred that, whereas in England and Wales study of the soil's "clay fraction" provides information of the kind most useful to the farmer, in the case of the northern Scottish soils, in which the "clay fraction" is always small, the nature and conditions of the minerals present in the "fine-sand fraction" call for further study by those who endeavour to assess the soil's agricultural value.

The chemistry of the soil's organic matter has been continuously studied at Rothamsted and Bangor, but the problem of the origin of humus has not yet been finally solved. An outline is given in the Report of the evidence for and against the lignin theory put forward by Page. The fate of fresh organic matter in soil and the causes that lead to its loss are now being investigated by Crowther and his colleagues at Rothamsted.

Soil Surveys and Soil Mapping.—A Soil Correlation Committee, set up by the Department of Agriculture, has so far identified and described about 150 soil series in England and Wales, and about 80 in Scotland. Each "soil series" recognised by the Committee includes within it all soils essentially similar in respect of parent material, mode of formation, topographical position and drainage conditions. The soil series are further subdivided into classes according to their texture. All the conditions responsible for a soil series are reflected in the soil's profile, or section, and the profile, which is studied either in natural sections or by boring with an auger, is therefore the unit to which the surveyor's attention is now mainly directed in the field.

Institutes for Soil Research.—A description is given of the history and activities of the Rothamsted Experimental Station and of the Macaulay Institute for Soil Research at Aberdeen.

PLANTS.—The Introduction to Part IV (pp. 44–77) summarises the improvements effected in plants, including wheat and fruit trees, by scientific breeding, and points out that breeding for resistance to disease is one of the most promising lines of work, although methods of direct attack or prevention, such as spraying, must long remain part of the necessary routine of the farmer and gardener. The workers at Rothamsted are studying the general aspects of the virus problem, and are in constant touch with the investigators of the Medical Research Council, who are dealing with virus diseases in animals and human beings.

The later part of this section gives a survey of the investigations now in progress at various institutions and research stations on plant physiology, plant breeding, horticulture, and fruit research, the virus diseases of plants and other diseases, and the improvement of grass-land.

Part V (pp. 78–87) is concerned with Animal Heredity and Genetics, and Part VI (pp. 88–97) with Animal Nutrition and Physiology. An outline is given of the work being done at the Rowett Research Institute, Aberdeen, and at the Cambridge Institute for Animal Nutrition. Part VII (pp. 98–156), on the Diseases

of Animals, describes the development of research in Great Britain during the early part of the present century, and then gives an outline of further advances in the field of animal pathology made by British workers. This is classified under the names of the various diseases, and concludes with a bibliography containing 59 references.

DAIRY RESEARCH (Part VIII, pp. 157–166).—With only limited funds at the disposal of the Council, it was held necessary to restrict Dairy Research Institutes to problems likely to yield results either of fundamental theoretical interest or of practical economic importance. Recent researches of most importance from the dairying point of view include the work that has shown the high nutritional value of young grass, and the need by cattle of a balanced ration containing both vitamins and mineral salts. The causes of loss of cows from dairy herds have been studied at various institutes; the average length of the milking life of cows works out at the surprisingly low figure of about 4 years. Other points investigated include the cost of production of "ordinary" and "special" milk, the physiology (including the genetics) of dairy cattle, the inheritance of milking properties, and statistical studies of the factors controlling the yield and quality of milk.

Reference is made to the fact that since 1931 evidence has been accumulating to show the value of the determination of the freezing-point as a test for the adulteration of milk with water.

Much discussion has taken place on the subject of the relative value of raw and pasteurised milk (*cf.* Report of the Committee of the Economic Advisory Council on Cattle Diseases. H.M. Stationery Office, Cmd. 4591).

Details are given of the work that has been done and is in progress at the Dairy Research Institutes.

PART IX (AGRICULTURAL ENGINEERING, pp. 167–173) deals with the work that is being done at the Institute for Research in Agricultural Engineering at Oxford, where agricultural machinery is tested and problems such as those connected with crop drying are investigated.

PART X (pp. 174–178) gives a description of the use of STATISTICAL METHODS at various Research Institutes, and the Report ends with a Conclusion by the Chairman of the Agricultural Research Council (the Rt. Hon. Lord Richard Cavendish). Appendix I gives the Charter creating the Agricultural Research Council; Appendix II is a note on administrative arrangements; Appendix III gives the personnel of the Committees of the Council; Appendix IV gives a summary of the grants sanctioned by the Council. There are three indexes—the first of personal names, the second of Government Departments, Institutions and other bodies, and the third of scientific subjects.

Union of South Africa

DEPARTMENT OF AGRICULTURE

ANNUAL REPORT OF THE CHIEF OF THE DIVISION OF CHEMISTRY FOR THE YEAR ENDED JUNE 30TH, 1933

IN his Annual Report Dr. St. J. C. O. Sinclair, F.I.C., gives an outline of the work carried out by the Division of Chemistry. In addition to its work for the Department of Agriculture, the Division also undertakes, as part of its regular routine, chemical work for the Departments of Public Health, Justice, Finance (Customs and Excise) and Mines and Industries. In addition, the Division is charged with the conduct of soil surveys required by the Department of Irrigation. The Division maintains three institutions—at Pretoria, Johannesburg and Capetown, respectively—and is also concerned with the work of the chemical sections of the four schools of agriculture.

PASTURE PROBLEMS.—*Feeding Value of Grasses of the Digitaria Species.*—At Pretoria the Division collaborated with the Division of Plant Industry in investigations relating to the feeding value of certain grasses (*Digitaria* species) at various stages of growth, and an account of the results has been published as a bulletin (*Science Bull.*, No. 126, by D. J. R. van Wyk). The most outstanding result of the experiments is that the young grass is relatively rich in phosphoric oxide and protein, irrespective of the progress of the season. On the other hand, the grass growing undisturbed alongside diminishes in P_2O_5 and protein as the season progresses. The phosphoric oxide figure is always much less in the mature dead grass than in the young grass, varying generally between one-half and one-third of the amount in the latter. In the best grass the amount seldom exceeds 0·5 per cent., which is very low. The lime-content increases as the plants mature, and seems to bear no relation to the P_2O_5-content. The crude protein is always greatest in the young plants, as usual. Most grasses reach values of over 10 per cent., but under 13 per cent. Extreme values of 3 per cent. are reached when the grass is dead. The following are typical analyses of samples of three species:

	Moisture in air-dried material Per Cent.	Percentages on dry sample							
		Ash	Fibre	Carbo-hydrates	Ether extract	P_2O_5	CaO	Protein	True protein
Digitaria Polevansii	7·8	6·90	36·8	46·2	1·3	0·27	0·50	8·8	5·5
D. littoralis	8·5	11·1	38·5	38·7	1·3	0·40	0·87	10·4	6·3
D. geniculata	8·2	10·9	36·3	44·0	2·1	0·35	0·77	6·8	5·8

UNIT VALUES OF CONSTITUENTS OF FERTILISERS AND FARM FOODS.—For a number of years the costs of fertilisers and farm foods have been discussed in an article in the July issue of *Farming in South Africa*, and each year the tests are brought up to date.* The system of valuation is fully explained in an article by Mr. C. O. Williams, published in the Journal of the Agricultural Department.†

In calculating these unit values it is assumed that insoluble phosphoric oxide has half the value of the soluble phosphate in any particular class of fertiliser, and the assumption agrees fairly well with the actual market price of the fertilisers. The values of the water-soluble and citric-soluble phosphate in superphosphate are taken to be equal—an assumption that agrees with the market value for citric-soluble phosphate in other fertilisers. For bone fertilisers the assumption is only

* See *Bulletins: Division of Chemistry Series*, No. 126, for 1933, and No. 133, for 1934 (by A. J. Taylor), from which the details abstracted here have been taken.

† Reprints can be obtained from the Division of Chemistry, Pretoria.

approximately correct, and it is also true that this insoluble phosphate becomes available in the soil more readily than the insoluble phosphate in such fertilisers as superphosphate or basic slag. The system of unit values applied to farm foods is based on the "carbohydrate" value, in which the proteins and the fat are both reckoned at two-and-a-half times the value of the soluble carbohydrates, together with an allowance of 2s. 6d. per unit of phosphoric oxide and 6d. per unit of lime for residual manurial value in foods rich in these constituents.

New Zealand

ANNUAL REPORT OF THE DOMINION LABORATORY

IN this, the Sixty-seventh Annual Report, the Dominion Analyst (Mr. W. Donovan, M.Sc., F.I.C.) gives a summary of the analyses and investigations undertaken for the different Government Departments. Of the 5345 samples examined at the main laboratory in Wellington, 3279 were for the Health Department. The totals for the branch laboratories were: Auckland, 2647; Christchurch, 2568; Dunedin, 1663. Most of these were milks submitted by the Health Department. The greater part of the work done for the police consisted in the examination of exhibits in cases of suspected poisoning, but it also included the analysis of materials in connection with criminal investigations.

ALCOHOL IN URINE.—A sample of urine received in connection with a death from suspected alcoholism contained 0·52 per cent. (by vol.) of alcohol. This was considered to indicate that the deceased died from alcoholic poisoning.

ARSENIC IN EXHIBITS DERIVED FROM GLASS BOTTLES.—Traces of arsenic in certain exhibits were found, after extensive investigation, to be derived from the glass of the bottles in which the material had been collected.

COUNTERFEIT COINS.—An interesting investigation was made in connection with the manufacture and uttering of counterfeit coins. Analyses showed that uttered coins and some found in the accused's house were of the same composition. The accused denied that the uttered coins had been made by him, but comparison of enlarged photographs of both sets of coins showed that they had all been made in the same mould. The accused was convicted.

BREAD WITH "REDUCED STARCH."—Samples of bread advertised as "Starch reduced—Protein increased" were examined. This bread was sold in loaves weighing not more than 1 lb. 9 oz., as against 2 lb. for ordinary bread, but owing to the fact that they had a greater volume in proportion to their weight than ordinary bread, the loaves looked heavier than they really were. In the preparation of the bread a certain proportion of flour from which starch had been washed was mixed with ordinary flour. The bread contained slightly less starch than some of the ordinary white bread on the market, but the advantage of this is doubtful. The protein present was 11·3 per cent. by weight, calculated on the dry material. Straight-run flours contain from 9 to 15·1 per cent. of protein on the dry basis. Hence, by using selected flour, bread containing considerably more protein than 11·3 per cent. could be made in the ordinary way, if desired. From a dietetic point of view this special bread would not be superior to average well-made ordinary white bread.

"BREAD IMPROVERS."—Several so-called "bread improvers" were examined and found to contain mineral salts. Bakers were warned against the use of such "improvers," which are not permitted by the New Zealand regulations.

PYRETHRUM FLOWERS GROWN IN NEW ZEALAND.—Samples of flowers from pyrethrum (*P. cineriaefolium*) grown in the North Auckland District were tested for their insecticidal value by determining the pyrethrin-content. Flower-heads grown from the Dalmatian variety of pyrethrum contained 0·33 per cent. of pyrethrins, and a specimen from the Japanese variety contained 0·74 per cent. The Japanese variety has been introduced into America, where it is growing successfully, and could no doubt be grown in New Zealand.

POISONOUS PRINCIPLE OF RAGWORT.—Preliminary work has been undertaken with a view to isolating and characterising the chemical nature of the poisonous principle in ragwort (*Senecio jacoboea*). About 0·15 per cent. of an alkaloid in the crude state was isolated from the air-dried plant. Large quantities are now being separated, in order to make physiological tests on the pure alkaloid and to study its chemical nature and properties. It is not definitely known whether the alkaloid is actually responsible for the poisoning of stock by ragwort.

KAURI-GUM.—The standardised resin obtained by the solvent process worked out in the Wellington laboratory is in the form of a dry granular powder, entirely free from foreign material. Reports received from European manufacturing firms who were supplied with bulk samples indicate that a ready market awaits the purified gum. Specimens of various grades of crude kauri-gum have been investigated as to their solubility and behaviour when subjected to the purifying process. Experiments on the esterification of the pure material are proceeding. Samples of resin associated with lignitic coal from Otago and Southland were found to be kauri-resin of high melting-point. The extent of the resin-bearing beds should undoubtedly be determined.

ANTIMONY IN ENAMELWARE.—As the result of reports from Great Britain of certain cases of antimony poisoning due to the use of enamelware in preparing an acid drink, it was thought advisable to examine the various brands of such ware sold locally, and especially kitchen utensils intended for use in the storage, preparation or cooking of foods. With several brands dangerous amounts of antimony were dissolved from the enamel by acid foods.

PITTING OF COPPER IN CONTACT WITH RUBBER AND KEROSENE.—A corrosion problem was investigated for the post and telegraph department. The copper anode of a transmitting valve cooled by circulating kerosene was found to be badly pitted where it was in contact with a rubber washer. The kerosene was discoloured, but sulphur and acidity were low. A sample from the tank, after stirring, contained 0·0081 per cent. of suspended matter, in which was 0·0052 per cent. of inorganic matter. This contained some copper, but much more zinc, showing that the copper salts formed by corrosion of the copper anode had attacked the galvanised coating of the tank. Corrosion tests showed that the kerosene became very dark when heated in contact with copper and pieces of the rubber washer. The copper was covered with a black deposit, and badly pitted. The discoloured kerosene also had the same effect on a copper sheet over which it was allowed to flow. On testing rubber from a washer of good quality in the same way, it was found that the kerosene was only slightly discoloured, the deposit on the copper was much smaller, and there was no pitting. It was clear that rubber of poor quality was the cause of the corrosion. Although copper catalyses the oxidation of rubber, rubber of good quality, preferably containing anti-oxidants, should be fairly resistant.

Standard Specifications for Solvents

THE British Standards Institution has issued specifications for the following eight industrial solvents:

Dibutyl phthalate (No. 573)	Hexachloroethane (No. 577)
Diethyl phthalate (No. 574)	Technical acetic acid (No. 578)
Carbon tetrachloride (No. 575)	Technical ether (No. 579)
Glacial acetic acid (No. 576)	Trichloroethylene (No. 580)

These specifications, which have been drawn up by the technical committee of the Chemical Division of the B.S.I., under the chairmanship of Dr. J. Vargas Eyre, prescribe tests and limits for specific gravity, acidity, alkalinity, distillation, etc., these limits having been fixed after consultation and agreement with the principal manufacturers and users of the solvents.

Copies of the specifications may be obtained from the Publications Department of the British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2s. 2d. each, post free.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Bromates in Flour. J. Kulman. (*Z. Unters. Lebensm.*, 1934, **68**, 375–377.)—The flour is mixed with chloroform and centrifuged. The upper layer of flour is then removed, the bromate being deposited on the bottom

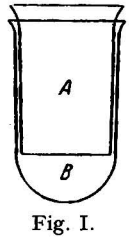


Fig. I.

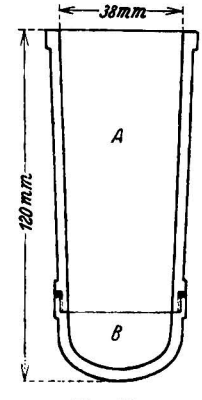


Fig. II.

of the tube. If necessary, further quantities of the flour may be added and the process repeated until the residue of bromate becomes appreciable. The bromate is then reduced with nascent hydrogen to bromide, which is detected by means of the red tetrabromofluorescein formed with an acid solution of fluorescein and a

drop of chlorine water (*cf.* Baines, ANALYST, 1928, **53**, 178). The method is applicable only when the bromate is present as crystals in the flour. For the centrifuging it is convenient to use a tube B (Fig. I) into which is ground a sleeve A. The flour may then be removed with B, the bromate and chloroform collecting in A.

For the determination of the bromate, use may be made of a bronze centrifuge tube constructed in two parts, A and B (Fig. II); these are screwed together, with a rubber jointing inserted. Forty g. of the flour and 75 ml. of carbon tetrachloride are centrifuged for 5 minutes (2000 to 2500 r.p.m.). With very fine flour, traces of the bromate may not separate; the centrifugation is then repeated. The lower part B is unscrewed and its contents transferred, with the help of carbon tetrachloride, to a glass-stoppered Erlenmeyer flask, and then filtered through asbestos moistened with the tetrachloride in a Gooch crucible. The residue on the filter is freed from fat by washing with 30 to 50 ml. of carbon tetrachloride and then returned to the Erlenmeyer flask, the walls of which are rinsed down with 30 ml. of water. After addition of 10 ml. of 2 per cent. potassium iodide solution and 10 ml. of 10 per cent. hydrochloric acid, the closed flask is left for 5 minutes. Five ml. of starch paste are added, and the liquid over-titrated with 0·01 *N* thiosulphate solution and back-titrated with 0·01 *N* iodine solution; 1 ml. of 0·01 *N* thiosulphate ≡ 0·28 mg. of potassium bromate. In presence of persulphate or iodate, a separate portion of the flour is treated and the persulphate determined either iodimetrically or colorimetrically; iodate is determined as in edible salt. Details of the procedure will be given later. T. H. P.

Flavine in White Wines. L. Genevois. (*Bull. Soc. Chim.*, 1934, **1**, 1504–1505.)—White wines exhibit a faint white fluorescence, which is readily observable in ultra-violet rays (Wood's lamp), and is attributed partly to the presence of flavine and its photo-derivative, lumiflavine. Zymoflavine, obtained from bakers' yeast either by extraction with methylal or by autolysis, cannot be extracted from its aqueous solution by hydrocarbons or their chloro-derivatives, which cause no reduction in the fluorescence of the liquid. Extraction of a white wine (from the Bordeaux district) with trichloroethylene, however, yielded an extract which, after filtration, showed a faint blue fluorescence and, on distillation, left a fluorescent solution. Three such extractions removed all this fluorescent substance. The residue of the wine was then treated by Kuhn's method for the detection of flavine: when the liquid was made alkaline, exposed to the light of a mercury-vapour lamp for 45 to 60 minutes, rendered acid again, and extracted with trichloroethylene, a fluorescent extract was obtained. Hence, there seems no doubt that the wine contained a flavine in small amount. That the substance extracted from the non-irradiated wine by trichloroethylene is identical with lumiflavine is, however, not yet proved. T. H. P.

Detection of Margarine and Hardened Oils in Foodstuffs. J. Grossfeld and J. Peter. (*Z. Unters. Lebensm.*, 1934, **68**, 345–358.)—The use of coconut butter and similar fats in margarine has greatly diminished in Germany, and the best way of recognising margarine is by means of the hardened oils (iso-oleic acid)

it contains. Such oils may be detected in edible fats by the following semi-micro-method: 500–550 mg. of the fat are boiled for 10 minutes in a 50-ml. Erlenmeyer flask under a reflux condenser with 5 ml. of alcoholic potash (40 ml. potassium hydroxide solution of sp.gr. 1·5 and 40 ml. of water, made up to 1 l. with 95 per cent. alcohol). The resulting soap solution is treated with 20 ml. of alcoholic lead acetate solution [50 g. of crystallised lead acetate, 5 ml. of 96 per cent. acetic acid, and 80 per cent. (vol.) alcohol to 1 l.], 1 ml. of 96 per cent. acetic acid and 3 ml. of water, the precipitate formed being dissolved by heating under a reflux condenser. After the corked flask has been left at about 20° C. for 2 hours, the precipitate is collected on a small glass-filter crucible (Schott & Gen. 10G/3), washed with 11 to 12 ml. of 70 per cent. (vol.) alcohol (previously used to rinse out the Erlenmeyer flask), and finally pumped as dry as possible.

The crucible and precipitate, with the filter-disc uppermost, are transferred to a suitable extraction apparatus; 0·6 ml. of 96 per cent. acetic acid is poured on to the disc and, with use of the Erlenmeyer flask, extraction with 20 ml. of the lead acetate solution is continued until the precipitate is dissolved. The boiling should be so vigorous that part of the liquid spurts into the extraction space and so facilitates the solution. The hot liquid is treated with 2 ml. of cold water and energetically shaken, any precipitate forming being dissolved by a short heating under a reflux condenser. After the flask has been left corked for 2 hours the precipitated lead salts of the fatty acids are again collected on the glass crucible, washed with about 12 ml. of 70 per cent. (vol.) alcohol and pumped as before. The crucible and precipitate are returned to the extraction apparatus, and the precipitate is dissolved in 20 ml. of a boiling mixture of 95 per cent. alcohol and 96 per cent. acetic acid in equal volumes. The hot solution of the lead salts is transferred to a 400-ml. Erlenmeyer flask, together with 10 ml. of the alcoholic-acetic acid mixture used for rinsing. The iodine value of the solid fatty acids is then determined as follows:—The cold lead salt solution is mixed with exactly 20 ml. of about 0·2 *N* iodine (25·4 g. of iodine dissolved in 96 per cent. alcohol to 1 l.), and the liquid then shaken with 200 ml. of water. After a few minutes the excess of iodine is titrated with 0·1 *N* thiosulphate solution. The iodine used up by a mixture of 15 ml. of 96 per cent. acetic acid with 15 ml. of 95 per cent. alcohol is determined similarly and used as a correction. (1 ml. of 0·1 *N* thiosulphate ≡ 14·12 mg. of iso-oleic acid.)

The above procedure includes two crystallisations of the lead salts, but a single crystallisation usually suffices to indicate the probable presence or absence of hardened fats and the consequent advisability of carrying out the double-crystallisation process. The limiting percentages (means in brackets) of iso-oleic acid found in edible fats with one crystallisation of the lead salts were: 2 hard fats, 24·8 to 38·8 (31·8); 9 margarine-fats, 9·3 to 17·0 (13·1); 11 butter-fats, 0·7 to 2·1 (1·6); 6 pigs'-fats, 1·5 to 2·0 (1·9); 5 ox-fats, 1·6 to 2·5 (2·2); 3 mutton-fats, 2·8 to 3·2 (2·9); cocoa butter, 1·3. When the lead salts were crystallised twice, the corresponding percentages were: 20·5 to 35·4 (28·0); 4·1 to 9·9 (7·3); 0·6 to 1·4 (0·9); 0·1 to 0·4 (0·3); 0·5 to 1·5 (1·1); 1·3 to 1·6 (1·5); 0·3.

Experiments with cocoa butter show that an addition of more than 10 per cent. of hardened fat is indicated by the increase in the iso-oleic acid value when the

lead salts are crystallised only once. With two crystallisations, 1 to 2 per cent. of the hardened fat gives a distinct rise in the iso-oleic acid figure. The natural content of iso-oleic acid in butter-, beef-, and mutton-fats disturbs the test only if more than 20 per cent. of butter-fat or more than 10 per cent. of beef- or mutton-fat is present in a mixture with cocoa butter. T. H. P.

Taint Production in the Fat of Chilled Beef. C. H. Lea. (*J. Soc. Chem. Ind.*, 1934, **53**, 391–392T.)—Deterioration of flavour in chilled beef-fat may be produced by micro-organisms, by odour absorption, or by oxidation. In the first case the rise in acidity, which almost invariably accompanies the deterioration in flavour, varies considerably owing to the different abilities of the organisms to hydrolyse fat. In samples taken from chill-rooms of retail shops a free acidity of 1·02 (as percentage of oleic acid) in one sample was associated with a worse flavour than an acidity of 1·36 per cent. in another, whilst in yet another sample the acidity was as high as 5·73 per cent., although there were no visible organisms. Visible mould was present in two samples with acidities of 10·51 and 13·71 per cent. An inoculation of fat from the interior of blocks of fresh beef scrotal fat with *Mucor* spores (a strain taken from mouldy beef-fat), produced a progressive rise in acidity in one case from 0 to 10·4 per cent. in 1 day, and in another to 10·4 per cent. in 16 days. Appreciable oxidation of chilled beef-fat stored in air does not generally occur unless there is undue exposure to light, but the use of carbon dioxide atmospheres has made storage practicable for much longer periods. However, after long periods bleached greyish or white patches may occur on the external fat of quarters, apparently owing to the conversion of oxyhaemoglobin into methaemoglobin, and all such samples examined had higher peroxide oxygen values than adjoining fat of normal appearance. D. G. H.

Some Indian Acorn Oils. S. V. Puntambekar and S. Krishna. (*J. Indian Chem. Soc.*, 1934, **11**, 721–726.)—The oils were extracted from the acorns of three of the 30 or more species of oak grown in India, *Quercus incana* Roxb., *Q. dilatata*, Lindl., and *Q. ilex*, Linn. The oil from the acorns of *Q. incana* was investigated in detail, since this is probably the most common and best known of all the species. The kernels (81 per cent.) were dried, and 16 per cent. of oil was extracted from them by means of petroleum spirit. The oils from the species of acorns examined were liquid, that from *Q. incana* was yellow, and those from the other 2 species were orange. The following analytical figures were obtained:—(*a*) *Q. incana*; (*b*) *Q. dilatata*, and (*c*) *Q. ilex*:—Sp.gr. at 25° C., (*a*) 0·9081, (*b*) 0·9084, (*c*) 0·9079; $n_D^{30°}$, (*a*) 1·4576, (*b*) 1·4588, (*c*) 1·4576; saponification value, (*a*) 192·2, (*b*) 188·4, (*c*) 189·9; iodine value (Hanus), (*a*) 81·5, (*b*) 90·3, (*c*) 83·0; acetyl value, (*a*) 14·8, (*b*) 21·1, (*c*) 17·4; Hehner value, (*a*) 96·1, (*b*) 88·2, (*c*) 94·9; acid value, (*a*) 13·0, (*b*) 22·2, (*c*) 8·5; unsaponifiable matter, (*a*) 0·8, (*b*) 2·3, (*c*) 0·9 per cent. The solid and liquid acids from the oil of *Q. incana* were separated by Twitchell's method, and their methyl esters fractionally distilled. They contained palmitic, 17·1; lignoceric (?), 0·9; and oleic acid, 82·0 per cent. The acetate of the purified sterol, separated from the unsaponifiable matter, melted at 126°–128° C., and appeared to be derived from sitosterol. D. G. H.

Malt Analysis. British and Continental Methods and the Inter-Relationship of Results. R. H. Hopkins, H. Lloyd Hind, and F. E. Day. (*J. Inst. Brewing*, 1934, **40**, 445–451.)—To convert the results of malt analysis by the Institute of Brewing Committee method (*id.*, 1933, **39**, 517) into the results which would be obtained by the usual Continental methods, *i.e.* Salzburg Convention for moisture, extract and colour and the Windisch–Kolbach method for diastatic power (see *Brewers' J.*, 1930, 237) the following calculations may be used: —Moisture, add 0·23 per cent.; extract, multiply by 0·802; colour, multiply by 0·086; diastatic power, multiply by 3·50, and then subtract 16. The respective standard errors of these figures are ±0·12, 0·005 and 0·008, the value for diastatic power being an approximation only. The factor for the extract converts English "lbs. per quarter" into the Convention units "per cent. Plato"; the Plato unit of a wort is the number of g. of wort-solids contained in 100 g. of wort, the relationships between sp.gr. and solids which hold for cane sugar being adopted for the purposes of a standard. This is considered preferable to the Balling unit. Variations in the ratio of the extracts determined by the two methods are attributed to the moisture-contents, and it is presumed that if the moisture exceeds 5 per cent., the malt will be inadequately ground in the Institute mill. The results were obtained experimentally with a wide range of malts, prepared according to English and Continental malting methods, but only two malts made from Californian barley and two from six-rowed barleys were included. Since the latter have a high grain-volume the Institute method for extract must give spuriously high results for them, and spuriously low results for malts made from two-rowed barleys; the Convention method avoids these errors. The essential points of difference between the two methods are indicated in each case. The Pollak–Egloffstein method for the determination of diastatic power has not been included in the comparisons, as it takes into account both the dextrinolytic and saccharifying components of diastase. Previous results (*J. Inst. Brewing*, 1934, **40**, 247) have shown that the Convention method of mashing gives, on an average, 0·08 to 0·15 per cent. more permanently-soluble nitrogen than the Institute method. J. G.

Analysis of Acriflavine, B.P. and Neutral Acriflavine. G. F. Hall and A. D. Powell. (*Quart. J. Pharm.*, 1934, **7**, 522–530.)—If the solubility requirements of the B.P. for acriflavine are to be satisfied, the product must contain not only the pure hydrochloride of 2 : 8-diamino-10-methyl acridinium chloride, but also an appreciable percentage of diamino-acridine hydrochloride. In confirmation of the results of Gailliot (*id.*, 1934, **7**, 63), 30 per cent. of the latter compound has been found to be necessary, although large quantities are undesirable. In any case, the present official limit test is unsatisfactory, and improvements are therefore suggested as follows :—*Qualitative.*—The formaldehyde test of the B.P. responds to proflavine, which is diamino-acridine sulphate; it requires the presence of sulphuric acid, and then gives a precipitate both with 90 per cent. acriflavine and with diamino-acridine. It is preferable (cf. *New and Non-Official Remedies*, 1930, p. 151) to add a few drops of a solution of formaldehyde and 5 ml. of a 10 per cent. solution of sodium nitrite to 5 ml. of 0·4 per cent. (w/v) test solution, and to filter after 5 minutes. The filtrate is red if acriflavine is present (distinction from euflavine

and diamino-acridine compounds). This is more sensitive than the test in which an effervescence with sodium bicarbonate is taken as an indication of the presence of acriflavine, and it may be adapted as a test for euflavine if this is first converted into acriflavine by the action of hydrochloric acid. *Quantitative.*—A solution of 0·5 g. of the sample in 20 ml. of water (30 ml. with neutral acriflavine) is neutralised with 0·1 *N* sodium hydroxide, with bromothymol blue as indicator. It is then diluted to 35 ml. and warmed to 60° C., and 25 ml. of the alkali are added, followed by 20 g. of sodium chloride. The precipitate is separated on a glass crucible on the following day, and is washed with 5-ml. portions of saturated sodium chloride solution at 5° C., until 5 ml. of washings require not more than 0·05 ml. of 0·1 *N* sulphuric acid to neutralise it to thymol blue. A mixture of the total filtrate and 26 ml. of the 0·1 *N* acid is boiled, cooled, and titrated with 0·1 *N* sodium hydroxide solution, with thymol blue as indicator (each ml. of alkali neutralised ≡ 0·0282 g. of diamino-acridine dihydrochloride). Precipitation as ferricyanide (*cf.* Powell and Hall, *Quart. J. Pharm.*, 1933, **6**, 389) is recommended for the determination of the "total flavines" (*i.e.* the total methylated and unmethylated derivatives of diamino-acridine) since it avoids the difficulty of the possible presence of nitrogenous decomposition-products. Gailliot's method (*loc. cit.*), which involves precipitation of the base with silver oxide, and subsequently, of diamino-methyl acridinium iodide with potassium iodide, is considered unsatisfactory. The following limits appear desirable:—"Total flavines" (as acriflavine), not less than 95·0 per cent.; unmethylated compounds (as diamino-acridine dihydrochloride), not more than 20·0 per cent.; Cl as acriflavine, not less than 95·0 per cent.; identification by the proposed colour test. J. G.

Analysis of some Mercurial Ointments. W. R. Heading. (*Quart. J. Pharm.*, 1934, **7**, 406–412.)—Existing methods are surveyed. In general, extraction of mercury with acid involves prolonged boiling to ensure that it is complete, and the disadvantages of extraction of the base material in organic solvents are losses due to protracted shaking and to the solubility of mercury salts in the solvent, and the difficulty of filtration of the finely-divided residue. The following procedures are suggested:—*General Method.*—A known weight of the sample is dissolved in 5 ml. of warm xylene or petroleum spirit in a dry round-bottomed centrifuge tube (1·9 × 10 cm.); the preparation should not come within 25 mm. of the top of the tube. The mixture is centrifuged until the supernatant layer is clear, and this is removed with a syphon, and the process is repeated with 3 further 8-ml. portions of petroleum spirit followed by 5 ml. of 90 per cent. alcohol. The residue is treated as follows:—For *Unguentum Hydrargyri, Ung. Hydrarg. Compositum, Oculentum Hydrarg. Oxidi*, and all ointments containing uncombined oxides of mercury.—The alcohol should have been drawn off to within 12·5 mm. of the suspension; the remainder is then removed by evaporation, the residue is dissolved in warm nitric acid, the solution being transferred to a flask and titrated with 0·05 *N* sodium thiocyanate as in the official assay of yellow mercuric oxide; the amount of sample taken should be equivalent to 0·15 to 0·2 g. of metal. For *Ung. Hydrarg. Ammoniatum.*—The moist residue obtained from 1 to 2 g. of sample is transferred to a flask, and the tube is rinsed with alcohol or acetone,

followed by 3 ml. of a 10 per cent. solution of potassium iodide. The official assay for ammoniated mercury is then carried out after addition of 3 g. of potassium iodide. With *Ung. Hydrarg. Subchloridi.*—The moist residue obtained from 0·75 to 1·5 g. of sample is treated as described for ammoniated mercury, with the omission of potassium iodide, and the official assay for subchloride of mercury is completed; it should not be necessary to add more than 30 ml. of 0·1 *N* iodine solution. The advantages are economy of time (an assay can be completed in 25 minutes) and material, and avoidance of fumes of acid or of hydrogen sulphide. The percentage errors found for the 3 types of ointment mentioned above were 0·13 to 2·13 (as Hg or HgO), 0·72 (as $HgNH_2Cl$) and 0·62 (as HgCl), respectively. The method is suitable for any ointment so long as the active constituent has a sp.gr. higher than that of petroleum spirit, is insoluble in neutral organic solvents, is not combined chemically with the basis of the ointment, and can be assayed accurately in the pure state. J. G.

Distribution of Nicotine in Raw Tobacco. T. B. Andreadis and E. J. Toole. (*Z. Unters. Lebensm.*, 1934, **68**, 431–437.)—The distribution of the nicotine in the leaves of a number of tobaccos from northern Greece (Macedonia and Thrace) has been examined. Increase in the nicotine-content is observed on passing from the middle leaves of the plant to either the lower or the upper leaves. Within any one of these three groups of leaves, a certain parallelism exists between the colour and the nicotine-content of a tobacco of a particular sort derived from a definite locality in any one season, the content increasing with the depth of colour of the leaves. In one and the same leaf, the proportion of nicotine increases from the median vein to the edges and from the base of the leaf to the tip, which is the richest in nicotine. T. H. P.

Biochemical

Comparison of the Pepsin and Rennin Activities of the Gastric Secretion of Different Animals. H. Holter and B. Andersen. (*Compt. rend. Lab. Carlsberg*, 1934, **20**, No. 8, 1–18.)—The pepsin and rennin activities of secretions from the stomachs of a number of mammals have been determined by the methods previously described (*id.*, 1933, **19**, No. 19; *Biochem. Z.*, 1932, **255**, 160; 1933, **262**, 99) and expressed in arbitrarily-defined but comparable units. The ratios (Q) of these values showed very small individual variations for each species of animal and were, for calves, 0·13 to 0·21; adult cows, 1·6; children, 2·7; adults, 2·5; puppies, 11·5; adult dogs, 12·5; adult pigs, 0·50; Merck's pepsin, 0·34; crystalline pepsin, 0·84. In the case of calves and dogs they are in agreement with the results of Hammarsten (*Z. physiol. Chem.*, 1910, **68**, 119) when these are expressed similarly. The big difference in Q in these two cases may explain differences in opinion as to the identity of pepsin and rennin, since some have been based on experiments with the former and some with the latter. Further evidence was obtained of the difference previously noted between the enzymes from calves and those from other animals, the chymosin component being less stable to acid than the pepsin component in the former case; the rate of destruction of chymosin

increases with decrease in *p*H value. The general validity of the hypothesis, that enzymes with a particularly powerful rennin action are typical of the ventricular function of infant mammals, is considered to be disproved by the fact that the stomach-enzymes from human adults and children are very similar, but differ from those from calves. It is concluded that the stomach secretions of infant mammals can be divided into two groups, one of which (typified by the calf) secretes a rennin enzyme (Hammarsten's chymosin) differing from pepsin and separable from it, and decreasing in amount with increasing age. In the other group (*e.g.* human beings and probably dogs) the value Q is similar for infants and adults, and cannot be displaced by chemical attack; chymosin is absent. J. G.

Extraction of Zymoflavine by means of Methylal. L. Genevois and L. Espil. (*Bull. Soc. Chim.*, 1934, **1**, 1498–1502.)—The zymoflavine extracted from yeast autolysate by Warburg and Christian (*Biochem. Z.*, 1932, **254**, 348; 1933, **257**, 492 and **266**, 377) may be more easily obtained as follows: 500 g. of fresh bakers' yeast, cold if possible, are shaken with 1 l. of distilled methylal (see p. 113) for 30 minutes, and the clear solvent is afterwards separated and distilled. The aqueous residue in the distilling flask amounts to about 100 ml. and contains the lipids in suspension. The lipids may be obtained by extracting this residue with ether and distilling the ethereal extract; the yield is several grms. per kg. of dry yeast. The residual pasty yeast, saturated with methylal, is left in contact for 30 to 60 minutes, with occasional shaking, with 1 l. of water saturated with methylal, which gives a single phase. After filtration, the methylal is distilled from the yellow filtrate in a vacuum at 30° C. As the flavine is affected on prolonged contact with methylal, this distillation is best carried out on 100- or 200-ml. portions of the filtrate as obtained. The turbid undistilled residue is fermented with fresh yeast (1 g. per 100 ml.) for at least 15 hours at room temperature to remove the sugars. The liquid is then freed from carbon dioxide by a current of air and shaken and left in contact for at least 30 minutes with about 3 per cent. of precipitated chalk. Filtration by suction then yields a clear, lemon-yellow or faintly orange liquid showing green fluorescence in ordinary light and pronounced white fluorescence in ultra-violet rays (Wood's lamp), and remaining unchanged for some weeks in a dark ice-chest. It still contains appreciable amounts of impurities, which may partly be precipitated by neutral lead acetate, but not, as Warburg stated, by the basic acetate. All the chemical properties of the flavines are shown by the solution, and the fluorescence is not affected by blocking the aminic functions with either formaldehyde or a bromoacetate or by oxidising the SH-groups with iodine in faintly acid solution.

The single extraction described above suffices to remove almost all the flavine from the yeast and serves to indicate the flavine-content, which appears to be of the order of a gram per kg. of dry yeast. Brewery yeasts, which multiply almost in absence of oxygen, are much poorer in flavine than bakers' yeast.

T. H. P.

Association of Fat-soluble Vitamins and Anti-oxidants in Plant Tissues. E. M. Bradway and H. A. Mattill. (*J. Amer. Chem. Soc.*, 1934, **56**, 2405–2408.)—It has been shown earlier that vitamin *A* or carotene, and especially

vitamin *E* as it exists in foods, are easily destroyed by oxidation in the presence of auto-oxidisable substances, and that their survival in such association depends, partly at least, on the protective action of naturally-occurring or added inhibitors. The presence of anti-oxidants in some vegetable oils and the isolation from lettuce of an anti-oxidant distinct from the vitamins and sterols suggest that such inhibitors may be the protective agencies of the labile fat-soluble vitamins in all plant tissues. Experiment now shows that the fat-soluble vitamins in tomatoes, carrots and wheat-germ oil are accompanied by inhibitors which prolong the induction period of auto-oxidisable fats. After the carotenoid pigments and sterols are largely removed from the unsaponifiable material, diphase distribution between 92 per cent. methyl alcohol and petroleum spirit separates the inhibitors from vitamin *E* in the case of tomatoes and carrots, but with wheat-germ oil both the inhibitor and the vitamin *E* are preferentially soluble in the petroleum spirit. From this observation and from the differing distillation ranges under diminished pressures it appears that the inhibitors in these three materials and in lettuce are all different. Similar evidence indicates the identity of the vitamin *E* derived from different sources. Only small amounts of this vitamin occur in carrots. Lycopene is not active as either vitamin *A* or *E*, but, like carotene, it is pro-oxygenic and shortens the induction period of auto-oxidisable fats. It seems likely that the inhibitors occurring in plants are not confined either to the unsaponifiable fraction of the plant lipids or to the aglucone portion of the glucosides. T. H. P.

Vitamin-*A* Content of the Herring. A. Scheunert and M. Schieblich. (*Z. Unters. Lebensm.*, 1934, **68**, 409–411.)—Rat nutrition experiments with Norwegian and Lerwick herrings show that sexually-mature herrings, whether fresh or smoked, contain vitamin *A* in their genital tissue, the roe being richer in this respect than the male gonads. T. H. P.

Biological and Titrimetric Determination of Vitamin *C*. H. Lund, B. Spur and L. S. Fridericia. (*Biochem. J.*, 1934, **28**, 1825–1828.)—The authors found that, on a vitamin-*C* free diet, guinea-pigs required about 0·7 mg. of ascorbic acid per day. Two samples of lemon juice contained 0·4 and 0·55 mg. per ml., respectively, and dried hips contained about 1·5 per cent. of ascorbic acid. A comparison of these results with those obtained titrimetrically by the use of 2:6-dichlorophenolindophenol shows fairly good agreement; only with the dried hips did the biological method show a higher content, and this was probably due to the incomplete extraction of ascorbic acid by the titration solution. Notice is drawn to the variations in the vitamin-*C* content of lemon juice. S. G. S.

Bacteriological

Preservation of Stock Cultures of Micro-Organisms. A. C. Thaysen. (*J. Inst. Brewing*, 1934, **40**, 469–471.)—The author has found (ANALYST, 1924, **49**, 446) that (*a*) addition of calcium carbonate to a culture of a non-sporing bacterium in vigorous growth, or (*b*) drying a suspension of bacterial spores on clean sterile sand, preserves the viability of such cells or spores for at least 12 months. Results of viability trials on these original cultures are now reported.

B. phosphorescens, *B. Kützingianum*, the *Saccharomyces* species, *red torula*, *Penicillium glaucum* and *Aspergillus glaucus* had died, although they were alive at the end of the first 12 months' trial. *B. volutans* and *B. fluorescens liquefaciens* survived for about 2 years, and *Streptococcus haemolyticus* died after 2 weeks. *B. coli com. mesentericus fuscus, subtilis, amylobacter, acetoethylicus* and *paratyphi*, grass coli, *Streptococcus acidi lactici* and *Rhizopus japonicus* had survived for 12 years. The salient morphological and biochemical characteristics before and after the period of preservation are tabulated. J. G.

Water

Rapid Determination of Free Chlorine in Water. L. Leroux. (*Compt. rend.*, 1934, **199**, 1225–1227.)—For the determination of amounts of chlorine below 0·5 mg. per l., *e.g.* in drinking and swimming-bath water, the author proposes an application of the Denigès-Chelle reaction (*id.*, 1912, **155**, 1010), in which a violet colour is given by bromine and an aqueous sulphuric acid solution of magenta (fuchsin). *Reagent.*—Ten ml. of fuchsin solution (0·1 per cent. in water) are mixed with 100 ml. of sulphuric acid (5 per cent.). The mixture becomes colourless in 1 hour and is stable. *Method.*—To 50 ml. of the water contained in a Nessler glass is added a crystal of potassium bromide, and, when it is dissolved, 1 ml. of the reagent and 1 ml. of acetic acid are added. The violet colour produced reaches its maximum intensity in 15 minutes and is stable. The colour may be compared with that produced by a standard solution of chlorine. Since the colour is identical with that of very dilute potassium permanganate, it is suggested that for "field-tests" the colour may be matched by adding drops of *N*/500 permanganate to pure water contained in a Nessler glass of similar size, the amounts of permanganate required to match the colours developed by different amounts of chlorine having been determined in separate tests. The presence of organic matter such as urea (300 mg. per l.) and of nitrates (300 to 400 mg. of nitrogen per l.) was found to be without effect. S. G. C.

Organic

Use of Methylal as a Solvent in Analysis. L. Espil. (*Bull. Soc. Chim.*, 1934, **1**, 1502–1503.)—Methylal, $CH_2(OCH_3)_2$, is now prepared industrially, and the commercial product is contaminated only with a small proportion of methyl formate which, however, undergoes gradual hydrolysis at the ordinary temperature, and thus renders the liquid increasingly acid. The formate may be removed by leaving the methylal for some hours in contact with 0·4 per cent. of its weight of a mixture of potassium hydroxide and carbonate and subsequently distilling it. The distillate (b.p. 42° C.) is quite free from acid and, as a solvent, has two advantages over ether: (1) It is more readily soluble in water; at the ordinary temperature, 1 l. of water and 600 ml. of methylal form a homogeneous mixture, and 1 l. of methylal dissolves in 50 ml. of water. (2) It dissolves considerable proportions of many organic acids, but only traces, at most, of mineral acids. Thus, *e.g.* it serves to extract tartaric and malic acids from wines. For a number of organic acids the distribution coefficients [C_p = (concentration of the acid in

water) ÷ (concentration of the acid in methylal)] have been determined by shaking 20 ml. of a solution of the acid with 0·2 ml. of concentrated sulphuric acid and 80 ml. of methylal. The values of C_p obtained are as follows, the corresponding values for ether being given in brackets:—Lactic acid, 2·5 (11); succinic, 2·4 (6); citric, 10 (155); malic, 8·6 (71); tartaric, 14 (260). When sodium sulphate is added in order to lower the solubility of the methylal in water, still lower values of C_p are obtained.

Note by Abstractor.—Methylal is stated to have pronounced anaesthetic properties. T. H. P.

Colorimetric Test for Compounds containing CH, CH_2 and CH_3 Groupings contiguous to Negative Groups. M. Goswami, A. Shaha and B. Mukerjee. (*J. Indian Chem. Soc.*, 1934, **11**, 773–775.)—If 2 drops of approx. 2 *N* sodium hydroxide solution are added to 1 ml. of a 0·05 per cent. alcoholic solution of picric acid with subsequent addition of a small quantity of the substance under examination, a red colour results if the substance contains contiguous CH, CH_2 or CH_3 groupings in proximity to the negative groups CHO or CO; thus nitromethane, malonic ester, cyanoacetic ester, acrolein, benzylacetone all give a red colour. This picric acid reaction is general under the conditions described above, whereas Bitto's reagents (*Annalen*, 1892, **269**, 377) fail in many cases. D. G. H.

Comparison of the Susceptibilities of Oils and Fats to Oxidation. C. H. Lea. (*J. Soc. Chem. Ind.*, 1934, **53**, 388–391T.)—The fat is dispersed on filter papers so that a very large ratio of surface to weight is obtained. The filter papers, which are 5·5 cm. in diameter and are fitted with loops of cotton, are weighed, immersed in the oil, pressed between sheets of filter paper to remove excess of fat, weighed again, and rapidly transferred to the jars. The papers are suspended in the jars (2-lb. preserve jars with loosely-fitting lids, to the undersides of which glass hooks are attached), a number of which, complete with lids, have been allowed to reach the temperature of a large electric oven (100° C.). At suitable intervals of time a jar is removed from the oven, and the paper is transferred to a Pyrex test-tube; powdered potassium iodide and a mixture of glacial acetic acid and chloroform (20 ml.) are added, and the peroxide-content is determined. Temperature control is important. Typical curves are given for cod-liver oil, lard, leaf-lard, olive oil, cottonseed oil, beef brisket-fat, beef kidney-fat, butter-fat, castor oil, egg-oil and a vegetable cooking-fat. With beef brisket-fat the initial increase in peroxide-oxygen appears to be arrested for about an hour before rapid absorption sets in, and the same thing is observed, though less definitely, with cottonseed oil. The curve for egg-oil is unusual, in that the peroxide value, after increasing normally for about 4 hours, ceased to rise, and remained constant for the next 20 hours. Possibly the breaks in the curves are due to the action of anti-oxidants. D. G. H.

Anti-oxidants and the Auto-oxidation of Fats, II. H. S. Olcott. (*J. Amer. Chem. Soc.*, 1934, **56**, 2492–2493; *cf.* Mattill, ANALYST, 1931, **56**, 200.)—Forty compounds of various types have been examined with regard to their ability

to retard the auto-oxidation at 75° C. of lard, either alone or mixed with cod-liver oil. Only two of the compounds, *viz.* hydroxyhydroquinone and apionol (1:2:3:4-tetrahydroxybenzene) showed anti-oxidant activity comparable in degree with that of the simple polyphenols, pyrogallol, hydroquinone and catechol. The fact that hexahydroxybenzene, although very easily oxidised, has no anti-oxygenic action, emphasises the absence of any simple relation between reducing action and anti-oxidant activity, which seems to depend in some way on a lack of balance in the benzene molecule. Esterification of one or both hydroxyl groups of hydroquinone destroys its action, and the only ester found not completely inactive was pyrogallol monocarbonate. Alkylation proved not quite as destructive as esterification. Mattill's conclusion, that both hydroxyl groups must be bound to the benzene nucleus (*loc. cit.*), is borne out by the inactivity of saligenin, and that of *cis*-1:4-cyclohexandiol emphasises the important rôle of the aromatic ring in anti-oxidants. The quinones were much less active than the corresponding quinols, and maleic, tartaric, and citric acids showed no anti-oxygenic action.

T. H. P.

Chemistry of Arachidonic Acid and its Quantitative Determination. W. C. Ault and J. B. Brown. (*J. Biol. Chem.*, 1934, **107**, 615–622.)—Arachidonic acid $C_{20}H_{32}O_2$ is usually determined by adding bromine to an ethereal solution of a mixture of fatty acids or their esters, and weighing the precipitated octabromides. The arachidonic acid is then calculated by means of the formula:

$$\text{Per cent. of arachidonic acid} = \frac{(\text{polybromide number of mixed acids}) \times 100}{80{\cdot}4.}$$

This is open to suspicion on the ground that the acid prepared by the reduction of the octabromide is not the same as that in the natural fat, and also that linolenic and other highly-unsaturated acids are determined by the same method. It is suggested that the polybromide number of the methyl esters should be used, as the esters prepared by three different methods have been found to give polybromide numbers differing but slightly from each other. Methyl arachidonate may be prepared by fractionation of the methyl esters of suprarenal phosphatide fatty acids, by the lithium soap and acetone method, or by the reduction of methyl octabromo-arachidate. In the lithium soap and acetone method 100 g. of fatty acids are weighed into a 3000–ml. flask and dissolved in 400 ml. of anhydrous acetone. This solution is titrated with aqueous 5 *N* lithium hydroxide solution until neutral to phenolphthalein, and enough water is added to make the total aqueous solution up to 120 ml. To this solution 1500 ml. of anhydrous acetone are added, with stirring, and the flask is kept in ice for 4 hours. The insoluble soaps are then filtered off and washed twice with 90 per cent. acetone. The soluble soaps are decomposed with dilute hydrochloric acid, about half the acetone is removed by distillation, and the remaining solution is diluted with several volumes of water and finally extracted with ether. The extracted fatty acids are esterified with methyl alcohol, and the methyl esters are distilled under reduced pressure. If the reduction method of preparation is used, 1 kg. of the freshly-distilled methyl esters of the fatty acids is dissolved in 4 l. of dry ether and brominated at 0° C. with constant stirring, and the precipitated bromides are washed seven times by decantation

with cold ether. One hundred g. of the precipitate are then suspended in 1 l. of methyl alcohol and boiled with 100 g. of zinc dust and 1 to 2 ml. of concentrated hydrochloric acid under a reflux condenser for 6 hours. About one-half of the alcohol is then boiled off and the residue is centrifuged. The clear alcoholic solution is poured into water and acidified to decompose any zinc arachidonate. The methyl ester is then extracted with ether and separated. The ether is distilled from the ethereal layer, and the residue is again boiled under reflux with methyl alcohol containing dry hydrochloric acid gas. Finally, the solution is distilled under reduced pressure. The following table gives a summary of the analytical figures obtained on the esters prepared by the different methods:

Method of preparation	Mean mol. wt. (ester)	Iodine value	Approx. purity Per Cent.	Polybromide number	Polybromide number based on 100 per cent. purity
Fractionation three times ..	311·5	261·8	85	74·4	87·6
Lithium soap and acetone method on whole acids	319·2	286·2	90	76·2	84·7
Same followed by fractionation ..	318·5	304·5	95	81·0	85·2
Reduction of bromides	317·8	316·9	100	86·5	86·5
Reduction of bromides	317·8	315·4	100	84·3	84·3
Theory, methyl arachidonate ..	318·0	319·0	—	—	—

The formula suggested for calculating arachidonic acid is

$$\text{Per cent. of methyl arachidonate} = \frac{(\text{polybromide number of mixed methyl esters}) \times 100}{86{\cdot}5},$$

but the polybromide number of the acid or acids present must be known or determined before using the formula. S. G. S.

Linaloe Oil, Mexican and Indian. W. H. Simmons. (*Perf. and Essential Oil Record*, **1934**, **25**, 378–379.)—True linaloe oil is distilled from the wood of various species of the *Burseraceae*, but oil of inferior odour, distilled from the seeds and fruits of the trees, is also met with, sometimes in admixture with the wood oil. Until about 1910 Mexican dextro-rotatory linaloe oils were rare, and the average ester-content was some 10 per cent., but from 1911 onwards the ester-content has shown a marked increase, until at the present time even 25 to 30 per cent. of esters may be found. Similarly, dextro-rotatory oils occur more frequently than in former years. During the last few years very fragrant Indian linaloe oils, grown from Mexican seed, have come on the market. The Indian wood and seed oils are very similar, but their sp.gr. is higher, on the average, than for the Mexican oils; the optical rotation is almost invariably positive (between 0 and +2°); the refractive index is lower than with Mexican oils, and the ester-content is high, lying generally between 35 and 44 per cent., as linalyl acetate. The limits for the analytical constants of (*a*) 7 samples of Indian linaloe wood oil and (*b*) 6 samples of seed oils were:—Sp.gr. at 15° C. (*a*) 0·8887 to 0·8981; (*b*) 0·8878 to 0·8911; [*a*], (*a*) +1°0′ to +2°30′; (*b*) 0°18′ to +2°18′; $n_D^{25°}$, (*a*) 1·4612 to 1·4628, (*b*) 1·4600 to

1·4623; ester (as linalyl acetate), (*a*) 37·3 to 44·9 per cent.; (*b*) 31·5 to 44·1 per cent.; alcohols (as linalool), (*a*) 73·3 to 76·1, (*b*) 71·8 to 74·7 per cent.; solubility in 70 per cent. alcohol, (*a*) 1 in 1·5 to 1 in 2, (*b*) 1 in 2 to 1 in 2·5. D. G. H.

Action of Hot Concentrated Sulphuric Acid on Dyes. R. B. Forster. (*J. Soc. Chem. Ind.*, 1934, **53**, 384T.)—The separation of the various classes of dyes may be facilitated by a study of their behaviour with hot concentrated sulphuric acid. The classes behave in a more or less characteristic way, except that the indigoid and anthracene dyes give specific, rather than general, reactions. A very small quantity of dye is dissolved in cold concentrated sulphuric acid, the colour observed, and the temperature then gradually raised to the b.p.

ACTION OF CONCENTRATED SULPHURIC ACID ON DYES

Class of dye	Colour in cold conc. sulphuric acid	Reaction on heating
Nitroso	Golden-orange	Decolorised→ pale straw-colour on boiling
Azo	Yellow to green	Decolorised→ carbonises
Stilbene-azo	Magenta to bluish-red	Decolorised, very little carbonisation on boiling
Stilbene	Yellowish-red to blue	Decolorised, practically no carbonisation on boiling
Thiazole	Pale yellow to brownish-yellow	Slightly darker, carbonises only after prolonged boiling
Triphenylmethane*	Yellow to yellowish-red	Darker, carbonises very easily
Diphenylmethane	Colourless	Reddish, carbonises rapidly
Xanthene	Yellow to brownish-red	Redder→ paler→ carbonises on boiling
Oxazine	Red to blue	Darker→ carbonises
Azine	Green	Discharges and carbonises
Induline	Blue	Slightly paler, then carbonises
Thiazine	Green	Darkens→ carbonises
Quinoline	Yellow	Slightly paler, very little change even on prolonged boiling
Acridine	Pale yellow (fluorescent)	Slightly darker, (fluorescence disappears), carbonises only with difficulty

* Sulphonated triphenylmethane dyes give a redder shade and are more resistant to carbonisation.

D. G. H.

Analysis of Asphalt, Bitumen and Tar Materials used in Road Construction. D. M. Wilson. (*J. Soc. Chem. Ind.*, 1934, **53**, 924–929.)—An account is given of the occurrence, manufacture, and uses of asphalt, tar, etc., in road construction, and data on the properties of the materials are collected in tabular form. Some notes are added on methods of analysis in amplification of the standard methods. *Bitumen-content.*—Bitumen is determined by difference on extracting the bitumen in carbon disulphide. Non-inflammable solvents such as trichloroethylene or perchloroethylene may be employed, but filtration is slower than with carbon disulphide. Loss of fine particles by "creeping" during filtration of the extract may be avoided by sealing the funnel with a glass plate. With steam-rolled asphalt, which may contain up to 45 per cent. of 1-in. stone chippings, it is necessary to dissolve the bitumen from at least 3 kg. of the sample in order to obtain representative results. The "penetration value" of the bitumen recovered by evaporation of the solvent should be determined, as it shows whether the material has been overheated in course of manufacture. *Tarmacadam.*—Suitable apparatus, in which the tar may be extracted in naphtha and any water

present in the aggregate may be collected at the same time in a modified Dean and Stark tube, has been described (*Highways and Bridges*, 1934, **1**, Pt. 5, 11). The residual slag should be analysed for silica and lime-content. It has been found that if the ratio CaO : SiO_2 exceeds 1·4, the slag is liable to crumble. *Identification of natural asphalt rock.*—Natural asphalt, which is a limestone naturally impregnated with bitumen, is often adulterated with limestone in order to cheapen the material. On examination of the mineral aggregate, after removal of the bitumen, under ultra-violet light, the natural asphalt rock usually shows a light brownish fluorescence, whilst crystalline limestones show a dark brown colour; there are exceptions. Examination of the aggregate with a binocular microscope is also helpful, especially if the unknown material is compared with known rocks. The natural rock is usually porous and often contains fossils, whilst added limestone is generally crystalline. The aggregate may be dissolved, as far as possible, in cold hydrochloric acid, and the residue may be examined by separation methods involving the use of heavy liquids, *e.g.* bromoform. Some limestones yield a residue containing fluorite (heavy) and chert (light), which are not present in the more commonly used asphalt rocks. *Identification of Trinidad Epuré.*—The heavy minerals which can be separated from the mineral aggregate of Trinidad Epuré by means of bromoform include titanite, zircon, rutile and glaucophane; glaucophane, whilst usually present in small amount, is blue in colour, and is characteristic of Trinidad asphalt. *Identification of bitumens by colour value*: Bitumen may be identified by examination of the colour of a dilute solution in perchloroethylene (0·25 g. in 100 ml.) contained in a glass cell, 0·5 cm. wide; a Lovibond tintometer is employed.

CHARACTERISTICS OF BITUMENS

	Penetration at 25° C.	Colour value		
		Neutral tint	Orange	Yellow
(*a*) *Bitumen recovered from asphalt rocks :*				
St. Jean	79	1·4	6·3	32·3
Sicilian	76	2·4	7·1	40·5
Val de Travers	73	2·0	8·5	49·5
(*b*) *Bitumen recovered from Trinidad Epuré and its mixtures :*				
Trinidad Epuré	11	2·1	6·9	11·1
75 per cent. Trinidad Epuré 25 per cent. Texaco Flux	71	1·1	6·1	35·8
50 per cent. Trinidad Epuré 50 per cent. Venezuelan 45	36	4·5	11·0	44·5
50 per cent. Trinidad Epuré 50 per cent. Panuco 45	36	2·6	9·7	47·7
(*c*) *Asphaltic Bitumen :*				
Panuco	45	3·3	11·0	45·7
Light Mexican	40	7·2	12·8	49·0
Venezuelan	42	7·1	12·9	40·0

S. G. C.

Inorganic

Preparation, Storage and Use of Standard Carbonate-free Sodium Hydroxide Solutions. W. W. Kay and H. L. Sheehan. (*Biochem. J.*, 1934, **28**, 1795–1797.)—Solutions of sodium hydroxide which are carbonate-free down to dilutions of $N/100$ may be prepared by the interaction of solutions of barium hydroxide and sodium sulphate. The sodium sulphate solution is freed from carbonates by making it slightly acid and boiling, and excess of this solution is used, as the presence of sodium sulphate has no effect on titration. A description is given of a new arrangement for storing and using such a solution under conditions of minimum carbonate contamination. S. G. S.

Determination of Sulphur in Cast Iron. E. W. Colbeck, S. W. Craven and W. Murray. (*Foundry Trade J.*, 1934, **51**, 308–310.)—Methods depending on the evolution of sulphur compounds by acid have been found to be inaccurate when applied to cast iron, and with the wet oxidation method it was difficult to secure satisfactory results. An improved method is proposed, in which the finely-ground sample is acted upon by copper ammonium chloride solution, which rapidly dissolves out the iron and leaves the sulphur in the carbonaceous residue, from which the sulphur can then be readily extracted by bromine and hydrochloric acid, giving a solution in which the acid concentration may be suitably adjusted for the precipitation of barium sulphate. *Method.*—A 4-g. sample (passing 22-mesh B.S.S. sieve) is weighed out into a 350-ml. conical flask fitted with a ground-in glass stopper or with a rubber bung which has been previously boiled in successive portions of hydrochloric acid until the acid gives no reaction for sulphate or sulphide; 250 ml. of copper ammonium chloride solution (30 per cent. in water acidified with 5 per cent. of concentrated hydrochloric acid) are added, and the flask is stoppered and shaken. The insoluble residue is filtered off on a pulp filter and washed until free from iron salts with a solution consisting of 1 vol. of copper ammonium chloride solution with 5 vols. of water, and finally with water. The residue is extracted with a mixture of 50 ml. of water, 2 ml. of bromine, and 5 ml. of concentrated hydrochloric acid by heating on a water-bath for half an hour. Bromine is then boiled off and the liquid is filtered, the washing being done with cold water. The filtrate is diluted to 200 ml. and heated to boiling, and 10 ml. of 10 per cent. barium chloride solution are added. The precipitate is allowed to settle overnight, filtered off, washed with cold water and ignited. The cited results of tests on various samples of grey and white cast iron, obtained by this and other methods, are held to confirm the validity of the present method.
S. G. C.

New Method for the Determination of Small Quantities of Aluminium. Application to Vegetable Substances. P. Meunier. (*Compt. rend.*, 1934, **199**, 1250–1252.)—Photometric determination of the turbidity formed by cupferron with small amounts of aluminium in a solution of regulated pH value is proposed. Iron, copper, titanium, etc., which also give precipitates with cupferron, can be removed by previous precipitation with cupferron in more strongly acid solution, the precipitate being separated by extraction with chloroform. *Method.*—The

ash from 0·5 to 1·0 g. of the dry vegetable substance is dissolved in about 10 ml. of 0·6 *N* hydrochloric acid. The solution is filtered and a 5 per cent. solution of cupferron is added until the presence of an excess is shown by the formation of a whitish precipitate. The liquid is extracted by shaking with two successive portions of chloroform. To the clear aqueous solution, transferred to a 50-ml. graduated flask, 5 ml. of 20 per cent. ammonium acetate solution and 0·5 ml. of the cupferron solution are added, and the liquid is diluted to 50 ml. The flask is shaken for a few seconds. After 20 minutes, and again after 30 minutes, the opacity of the turbidity is measured by means of a Féry spectrophotometer or a photo-electric nephelometer. Aluminium solutions of known strength are employed as standards, and are treated in a similar manner. In test experiments, amounts of aluminium from 0·01 to 0·06 mg., added to 1 g. of vegetable matter, were recovered with an accuracy of 5 per cent. Other results obtained by this method have been confirmed by the gravimetric method of Bertrand and Levy (*Compt. rend.*, 1931, **192**, 525). S. G. C.

Precipitation of Aluminium by means of *o*-Hydroxyquinoline in presence of Iron, Nickel, Cobalt, Copper, Chromium, and Molybdenum. T. Heczko. (*Chem.-Ztg.*, 1934, **58**, 1032–1033.)—The method involves the conversion of the iron, nickel, etc., into complex cyanides, in which form they are not precipitated by *o*-hydroxyquinoline. *Method.*—To the solution of the alloy (0·5 to 1 g.) in *aqua regia* are added 8 to 10 g. of dissolved tartaric acid; it is diluted to 100 ml. and rendered ammoniacal; 5 to 10 g. of potassium cyanide are added, and hydrogen sulphide is bubbled in for 10 minutes in order to reduce iron to the ferrous condition, when it becomes converted into ferrocyanide. After 1 hour any precipitate of manganese sulphide, silica, etc., is filtered off. [Manganese sulphide is difficultly filterable, so that if appreciable amounts of manganese are present (more than 5 mg.), it is desirable to filter off an aliquot portion, re-filtering, if necessary, to obtain a clear solution. If much silica is present, some alumina is likely to be adsorbed on it, and it is therefore necessary to treat it as follows:—It is ignited in a platinum crucible; hydrofluoric acid and sulphuric acid are added, and the liquid is evaporated to dryness; the residue is fused with potassium bisulphate and dissolved in dilute sulphuric acid; a few g. of ammonium sulphate and a few drops of hydrogen peroxide are added, and the aluminium and any iron are precipitated with ammonia, methyl orange being used as indicator; the precipitate is filtered off, washed, and dissolved in dilute sulphuric acid; some tartaric acid is added, the solution is rendered ammoniacal and added to the main filtrate.] The filtrate is heated to boiling and a slight excess of a concentrated solution of *o*-hydroxyquinoline in alcohol is slowly added, with stirring. After 2 minutes the precipitate is filtered off on a sintered glass crucible, washed with warm water, and dried at 150° C. The weight of the precipitate, multiplied by 0·0587, gives the weight of aluminium present. *Modification for chromium alloys.*—As a very considerable quantity of tartaric acid is required to maintain tervalent chromium in solution, it is desirable to convert the chromium into chromate, as follows:—To the solution of the alloy in dilute sulphuric acid are added a few g. of ammonium persulphate and a few mg. of silver nitrate, and the solution is

warmed. When oxidation is complete and any manganese has been converted into permanganic acid, a few ml. of hydrochloric acid are added, and the solution is boiled and subsequently cooled. This solution is then treated as for non-chromium alloys. S. G. C.

Detection of Chlorine and Bromine in Gases or Solutions by Means of Resorufin. H. Eichler. (*Z. anal. Chem.*, 1934, **99**, 272–275.)—The solution of resorufin in alkali carbonate, of red colour with intense yellow-red fluorescence, yields with bromine tetrabromoresorufin, the alkali salts of which are blue; chlorine acts like bromine. For the detection of either, the solution containing sodium carbonate or bicarbonate, but not hydroxide or free acid, is treated with a minimum of reagent (0·1 g. of resorufin and 1·5 g. of sodium carbonate in 100 ml. of water). Substitution takes place almost instantly in the cold, a blue colour being obtained. An excess of reagent produces a yellow-red fluorescence; a large excess of halogen destroys the blue reaction product. For the detection of the halogens in air, etc., the gas is led through a dilute solution of the reagent; chlorine and bromine destroy the fluorescence. W. R. S.

Detection of Hydrosulphite and Nascent Hydrogen by Means of Resazurin. H. Eichler. (*Z. anal. Chem.*, 1934, **99**, 270–272.)—The reagent is a solution of 0·1 g. of resazurin or its sodium salt and 0·3 g. of sodium carbonate in 100 ml. of air-free water. The solution to be tested, which must contain free sodium carbonate, is treated with a minimum of reagent. If no hydrosulphite ($Na_2S_2O_4$) is present, the blue colour of the reagent and its brown fluorescence remain unaltered; otherwise, the colour is discharged in the cold. Further addition of reagent will then produce a red fluorescence, due to the conversion of the hydroresorufin into resorufin. Sulphites react sluggishly; thiosulphates do not reduce. Ferrous or stannous hydroxide reduces in the cold. In acid solution, thiosulphates or sulphites reduce the reagent acidified with sulphuric acid, as also do metals by producing nascent hydrogen. Stannous or titanous salts likewise decolorise the reagent; hydrochloric acid should not be present, as it forms chloro derivatives at higher temperatures. W. R. S.

Analysis of Reducing Sulphur Acids. E. Cherbuliez and H. Herzenstein. (*Helv. Chim. Acta*, **1934**, **17**, 1582–1587.)—*Determination of Hydrogen Sulphide.*—To the approximately neutral solution is added a suspension of precipitated cadmium carbonate, and the whole is shaken for half a minute, when the hydrogen sulphide reacts to form cadmium sulphide. The precipitate is filtered off, washed with water, and then stirred up with a little water and a slight excess of 0·01 *N* iodine solution. The excess of iodine is titrated with standard thiosulphate solution, starch being used as indicator. Hydrogen sulphide may thus be separated from sulphurous, thiosulphuric, and hydrosulphurous acids, which do not react with cadmium carbonate. *Determination of Thiosulphuric Acid.*—The reaction between sodium azide and iodine according to the equation $2NaN_3+2I=3N_2+2NaI$ is catalysed by thiosulphuric acid, and the extent of the reaction is proportional to the amount of thiosulphuric acid present; the thiosulphuric acid becomes simultaneously oxidised to tetrathionate. The following method is proposed:—To 5 ml. of the solution [? neutral: *Abstractor*] are added 0·2 g. of sodium azide and a

few drops of starch solution. Standard iodine solution (0·01 *N*) is added, drop by drop, with constant stirring, until the starch-blue persists for half a minute. The thiosulphate value of the iodine solution is determined by titrating a standard thiosulphate solution under similar conditions. Hydrogen sulphide, hydrosulphurous acid, and thiocyanic acid interfere. *Reactions of Thiosulphuric Acid in Dilute Solutions.*—(*a*) The lower limit for the detection of thiosulphates by acidifying and observing the turbidity of sulphur produced is about 0·001 *N*. (*b*) At *p*H 6 thiosulphuric acid is stable, and colloidal sulphur produced, *e.g.* by the action of iodine on hydrogen sulphide, dissolves readily in sulphurous acid, yielding thiosulphuric acid. *Detection of Sulphurous Acid.*—Sulphurous acid bleaches magenta (fuchsin), and when formaldehyde is subsequently added, the colour re-appears (Votoček, *Ber.*, 1907, **40**, 414); this reaction has been found sufficiently sensitive to detect 2 ml. of 0·01 *N* bisulphite solution per l. S. G. C.

Measurement of Atmospheric Sulphur Pollution by means of Lead Peroxide. B. H. Wilsdon and F. J. McConnell. (*J. Soc. Chem. Ind.*, 1934, **53**, 385–388T.)—The method for measuring pollution of the atmosphere due to the burning of coal, devised for the Atmospheric Pollution Research Committee of the Department of Scientific and Industrial Research, has now been in use for three years, and its general adoption has been recommended to co-operating local authorities. It consists in the determination of the sulphur dioxide present after absorption of the sulphur compound on a prepared surface of lead peroxide (ANALYST, 1933, **58**, 284). The lead peroxide is mixed with a 1 per cent. mucilage of gum tragacanth, which produces the required matt surface without reduction of porosity, and the resulting paste is applied to a cloth surface wrapped round a porcelain former. The ranges of proportionality between the rate of absorption and the concentration of sulphur dioxide and period of exposure were investigated, for the particular paste and type of cylinder, by placing cylinders in a small wind tunnel through which was passed a stream of air containing known quantities of sulphur dioxide, and it was evident that within the limits of experimental error the rate of absorption remains approximately linear, even when as much as 15 per cent. of the absorbent has been converted. Since wind velocity, as well as temperature, may have an effect and the method is for outdoor exposure, it is particularly important to establish a statistical relation by which the range of variation in the relation between lead peroxide sulphation and the volume concentration of sulphur dioxide may be assessed, rather than to rely on results obtained under artificial conditions. For small velocities the rate of absorption was found to vary inversely as the fourth root of the air velocities, and these variations, together with those due to temperature, have been estimated and compared with the range of variation calculated statistically from two years' observations, in the course of which both the volumetric and lead peroxide methods were used. The observed variation is greater than that attributable to wind and temperature, and is probably dependent on errors in the volumetric method and on differences in the exposure at the points of observation. The lead peroxide method provides a simple way of estimating prevalent concentrations of sulphur dioxide if exposures are so made that corrections may be applied for effects of wind velocity and temperature. D. G. H.

Microchemical

Apparatus and Methods for Micro-sublimation. R. Fischer. (*Mikrochem.*, 1934, **15**, 247–271.)—Various apparatus and methods for micro-sublimation are described, and, in particular, the author's improved model of the electrically-heated combined m.p. and sublimation block, which is provided with means for accurate temperature measurement, an automatic temperature regulator, and glass covers for sublimation under reduced pressure.

J. W. M.

Collected References. Electrographic Methods. R. Jirkovský. (*Mikrochem.*, 1934, **15**, 331–343.)—A summary of the methods, as used by different authors, and their applications, are described. The applications are mainly concerned with the examination of metals and alloys, when a metal plate is used as cathode and the metal under examination as anode (or *vice-versa*), and "spot" paper impregnated with a reagent for the metal going into solution is placed between the anode and cathode. References to 20 papers are given. J. W. M.

Spot Tests for Organic Compounds. III. F. Feigl and V. Anger. (*Mikrochem.*, 1934, **15**, 23–25.)—*Detection of Sulphonic Acids.*—Either a little of the solid substance or a drop of the test solution, evaporated to dryness in a porcelain micro-crucible, is heated with a few drops of thionyl chloride until fumes appear, after which two drops of a saturated alcoholic solution of hydroxylamine hydrochloride and a drop of acetaldehyde are added, and the mixture is rendered alkaline with 5 per cent. sodium hydroxide solution. After a few moments the mixture is acidified with alcoholic hydrochloric acid, and, finally, a drop of a dilute aqueous solution of ferric chloride is added; a brown to violet colour or precipitate indicates that a sulphonate was present.

The reactions that take place are expressed by the following equations:

$$R\mathrm{SO_3H} + \mathrm{SOCl_2} \rightarrow R\mathrm{SO_2Cl} + \mathrm{SO_2} + \mathrm{HCl}$$
$$R\mathrm{SO_2Cl} + \mathrm{NH_2OH} \rightarrow R\mathrm{SO_2(NHOH)} + \mathrm{HCl}$$
$$R\mathrm{SO_2(NHOH)} + \mathrm{CH_3CHO} \rightarrow \mathrm{CH_3C{\cdot}(NHOH)} + R\mathrm{SO_2H}$$
$$3\mathrm{CH_3CO(NHOH)} + \mathrm{FeCl_3} \rightarrow \mathrm{Fe[CH_3CO(NHO)]_3} + 3\mathrm{HCl}$$
$$3R\mathrm{SO_2H} + \mathrm{FeCl_3} \rightarrow \mathrm{Fe}[R\mathrm{SO_2}]_3 + 3\mathrm{HCl}.$$

When a sulphonic acid salt is being tested it should be evaporated with hydrochloric acid before treatment with thionyl chloride. Dyestuffs, the colours of which interfere with the observation of the test, may be decomposed with a few drops of bromine water. Amino-groups, which affect the conversion of the sulphonic acid into the chloride, may be decomposed with sodium nitrite. The *detection limit* is given for the following sulphonic acids:—Benzene chlorosulphonate, 12γ; naphthalene-β-sulphonic acid, 20γ; sulphanilic acid, 25γ; potassium p-benzene disulphonic acid, 10γ; "H" acid, 15γ; helianthine, 30γ. The colour-reaction with all these compounds is brown. J. W. M.

Spot Tests for Organic Compounds. IV. F. Feigl, V. Anger and O. Frehden. (*Mikrochem.*, 1934, **15**, 181–190.)—*Detection of Nitroso Compounds.* The Liebermann reaction (*Ber.*, 1882, **15**, 1529; 1883, **16**, 1473; 1887, **20**, 3231) and

the Baudisch reaction (*Ber.*, 1921, **54**, 413; 1922, **55**, 2702; 1929, **62**, 2699, 2706) have been adapted for use on the micro-scale as "spot" tests. For the Liebermann test a crystal of pure phenol and a few granules of the substance under examination are mixed in a micro-crucible and heated to melting. The fused mass is allowed to cool and treated with a few drops of pure sulphuric acid. A dark cherry-red colour is usually produced, changing on dilution and treatment with 4 *N* alkali, generally to blue. For the Baudisch reaction the most suitable prusso-salt to use as reagent is sodium pentacyanammino-ferroate ($Na_3[Fe(CN)_5NH_3]$), used in 1 per cent. solution. This compound is prepared by mixing sodium nitroprusside with three times its amount of concentrated ammonia; the mixture is cooled with ice and, after 24 hours, diluted with alcohol, filtered and washed. For the test, a drop of the solution under examination is mixed with a few drops of the reagent and allowed to stand for the colour to develop. The results obtained with certain nitroso compounds are given in the following table:

	Liebermann reaction		Baudisch reaction	
Compound	Identification limit	Colour change	Identification limit	Colour change
	γ		γ	
p-Nitroso dimethylaniline	0·5	red to yellow-green	0·15	green
p-Nitroso phenol	0·4	red to blue	0·15	dark green
α-Nitroso β-naphthol	0·5	red to blue	1	olive green
β-Nitroso α-naphthol	0·6	red to green	1	olive green
Tetrahydro β-nitroso-α-naphthol	0·5	red to green	—	no reaction
iso-Nitroso acetyl acetone	1	dark red to green-yellow	2·5	brown lilac
iso-Nitroso acetophenone	1	red to yellow	3	green

Detection of nitro compounds.—The Baudisch test, described above, can be used for nitro compounds after reduction to nitroso compounds. A drop of the solution under examination is mixed with a few drops of the reagent and a drop of 4 *N* alkali solution in a micro-crucible, and the test solution is reduced electrolytically, a nickel wire being used as cathode and a lead wire as anode, and the current passed for 10 to 30 minutes. If, on adding alkali before electrolysis, a colour-change occurs, a drop of 5 per cent. sodium thiosulphate solution is used instead of the electrolyte. A blank test should be carried out. The reaction is useful for differentiating different kinds of artificial musks. A table is given of 34 different nitro-compounds with the limit of identification and colour formed in each case. *Detection of organic hydrazine derivatives.*—Many hydrazine derivatives also react with sodium pentacyanammino-ferroate to give coloured products on standing. A table is given showing the colours in neutral and in alkaline solution and the identification limit obtained with 10 hydrazine derivatives. J. W. M.

Detection of Aldehydes and Ketones. II. R. Fischer and A. Moor. (*Mikrochem.*, 1934, **15**, 74–87.)—Further reagents are suggested for the detection of aldehydes and ketones by the formation of crystalline derivatives, and the determination of the m.p. of the derivatives under the microscope (*Mikrochem.*, **1933, 13**, 123; Abst., ANALYST, **1933, 58**, 569). The additional reagents are:—(i) *o*- and *m*-nitrophenylhydrazine, used mainly as a saturated solution in 15 per cent., and, sometimes, in 30 per cent. acetic acid; the solution, which should be kept in glass-stoppered bottles, is stable for only 3 or 4 days. (ii) *m*-nitrobenzene hydrazide (m.p. 152° C.) used in saturated solution in 30 per cent. acetic acid.

(iii) Semicarbazide (m.p. 96° C.), used as a saturated aqueous solution, or 2 g. are mixed with 2 g. of sodium acetate and dissolved in 6 g. of water; when the reagent solution becomes cloudy it should be discarded. (iv) Semi-oxamazide (m.p. 234° C.) used either as a saturated aqueous solution or dissolved in 30 per cent. acetic acid. This is a useful reagent, but the derivatives tend to be very volatile in the region of the m.p., which must therefore be determined with rapid heating (4° to 6° C. per minute). (v) Thio-semicarbazide (m.p. 183°–184° C.) is employed somewhat less frequently as a reagent; it is used either as a saturated aqueous solution or dissolved in 20 per cent. potassium acetate solution. Reactions of the following aldehydes and ketones with the reagents are described, and a table is given of the m.p. of the derivatives formed:—Formaldehyde, acetaldehyde, furfural, acrolein, *iso*-valeraldehyde, propionaldehyde, crotonaldehyde, benzaldehyde, *p*-chlorobenzaldehyde, cinnamaldehyde, salicylaldehyde, anisaldehyde, piperonal, cuminaldehyde, vanillin, acetone, acetophenone, chloracetophenone, carvone, menthone, thujone, methyl butyl ketone, and ethyl *iso*propyl ketone. J. W. M.

Test for Small Amounts of Fluorine. S. Kühnel Hagen. (*Mikrochem.*, **1934, 15**, 313–315.)—Very small amounts of hydrogen fluoride which are insufficient to etch glass surfaces change its quality slightly, so that sulphuric acid no longer runs over it smoothly, but agglomerates like water on a greasy surface. A small narrow test-tube is thoroughly cleaned with potassium dichromate completely dissolved in 1 to 1·5 ml. of hot concentrated sulphuric acid, which is run over the whole interior surface. A little of the solid substance to be tested for fluorine or a drop of the solution is added, and the mixture is boiled. In the presence of fluorides small or large flecks will be seen above the condensation boundary of the sulphuric acid on the glass from which the acid withdraws. When large amounts of fluorine are present this effect is instantaneous. The detection limit is 0·5γ of fluoride. Other halogens, sulphur compounds, nitrates, phosphates, carbonates, or salts of zirconium, titanium, uranium, or vanadium do not interfere. Iron and molybdenum compounds slightly reduce the sensitivity. Complex radicles such as BO_2' and SiO_3'' reduce the sensitivity to 5γ in the presence of 0·3 per cent. of SiO_3 or 0·5 molar BO_2. J. W. M.

Physical Methods, Apparatus, etc.

Fluorescence Test for Olive Oils. T. T. Cocking and S. K. Crews. (*Quart. J. Pharm.*, **1934, 7**, 531–534.)—The sample is treated with decolorising charcoal (B.D.H.) as described (*Pharm. J.*, 1934, **133**, 86; Abst., ANALYST, **1934, 59**, 652), and on the next day the clear supernatant oil is filtered and examined in a thin bottle of non-fluorescent glass in filtered ultra-violet rays (310 to 390$m\mu$). Genuine virgin olive oils, which had originally a deep golden-yellow fluorescence, became almost colourless and showed only a faint and dull blue fluorescence. The usual adulterants which have low Bolton–Williams values (arachis, sesame and tea-seed oils) and "refined" olive oils were all bleached, but retained their original blue fluorescence, which is usually taken as an indication of this form of

adulteration. Certain olive oils which have recently appeared on the market have an opaque dark purple or chocolate-coloured fluorescence before treatment, and it is suspected that this is due to the intentional addition of some substance to mask the blue fluorescence of the above adulterants. The charcoal treatment removed this masking fluorescence completely, leaving the blue fluorescence. Virgin olive oils which have been heated at 300° C. also show a blue fluorescence (*cf.* Musher and Willoughby, *Oil and Fat Ind.*, 1929, **6**, 15), which is not removed by charcoal. About 5 per cent. of arachis or tea-seed oil is detectable by the method; intense fluorescence may be recorded by the Lovibond tintometer.

J. G.

Fluorescence and Detection of Rhapontic Rhubarb. T. E. Wallis and E. R. Withell. (*Quart. J. Pharm.*, 1934, **7**, 574–580.)—Further details are given of the test previously described (*Pharm. J.*, 1934, **133**, 90; Abst., ANALYST, 1934, **59**, 652). The prepared strips of cellulose wadding paper, saturated with the alcoholic tinctures of the sample and of genuine Chinese rhubarb and dried for 20 minutes on a sheet of glass in the dark, are examined beneath the ultra-violet lamp as rapidly as possible. The violet fluorescence of rhapontic rhubarb gradually disappears on exposure of the strips to ultra-violet light or to diffused daylight, and is completely replaced in each case by the same pale yellow fluorescence after 20 minutes and 4 days, respectively; the effect is less marked on the unexposed side of the strip, and with powdered rhubarb. The intensity of the fluorescence of the strips is reduced visibly after 30 minutes at 70° C., and to a considerable extent after 18 hours; it is also reduced if the maceration is carried out in daylight. Filter papers used for the strips vary in appearance in ultra-violet light, those containing cotton fibres being blue, whilst wood cellulose does not fluoresce and is preferred for the test.

(*Abstractor's Note.*—The fluorescence of paper fibres depends on the nature of the treatment they have undergone rather than on the origin of the fibres. It also alters when the paper is exposed to ultra-violet light, to daylight, or to heat, and this may influence the changes noted above.)

J. G.

Reviews

HANDBOOK OF CHEMISTRY. By N. A. LANGE, Ph.D. Pp. 1265. With Appendix of Mathematical Tables and Formulas by R. S. BURINGTON, Ph.D. Pp. 248, and Index, pp. 29. Sandusky, Ohio: Handbook Publishers, Inc., 1934.

This book consists chiefly of tables of chemical and physical constants, and it also contains a mass of information which should render it useful as a work of reference in several branches of pure and applied science. Recent investigations, where available, have been laid under contribution, and the work deserves high praise both for what is included and for what is omitted.

The tables of physical constants of inorganic and of organic compounds are very full, occupying 350 pages of fairly close print; the references to "Beilstein,"

which are given for most of the organic compounds, link the book to the whole field of organic chemistry. The data for fats, oils and waxes, alkaloids, glucosides, and resins are given very fully in separate tables. Electrometric and colorimetric methods for determining pH values are described.

In the tables showing the relations between specific gravity, percentage content, hydrometer readings, etc., of aqueous solutions, degrees Baumé are given according to the formula for the American scale. So long as the Baumé hydrometer remains in vogue for industrial purposes, chemists must, perforce, use it. As the author points out, however, there are about 36 Baumé scales in use; the suppression of at least 34 of them by international action is certainly called for.

Considering the scope of the book and the enormous amount of information that it contains, the errors observed are very few. In the brief description of the elements on pp. 20—42, oxides and hydroxides are in some cases included amongst the "salts" formed by the element; on p. 35 "Niton" is misspelt "Nitron," and on p. 512 witherite is stated to be barium sulphate. Helium was isolated in 1895, and not in 1898, as stated on p. 27. Alabamine (eka-iodine), illinium and virginium (eka-caesium) are included amongst the elements, but for alabamine and virginium, at least, the claim to such inclusion can hardly be regarded as established, and the statement under the heading "Alabamine" on p. 20 that "The discovery of this element marks the end of the search for new elements from numbers 1 to 92 . . ." is rather a rash one.

L. EYNON

THE PRACTICE OF ABSORPTION SPECTROPHOTOMETRY. By F. TWYMAN, F.Inst.P., F.R.S., and C. B. ALLSOPP, M.A., Ph.D. Second Edition. Pp. 144, 45 Figs. London: Adam Hilger, Ltd. Price 12s. 6d. net.

The new edition of this very useful book differs from its predecessor mainly in two features. Part I is new; it is a short treatise on the general principles of the practice, mainly by Dr. Allsopp. Part II constitutes a new and up-to-date edition of the original work, by Mr. F. Twyman.

The earlier section deals with the nature of absorption, illustrated by simple absorption spectra of various glasses, solvents, etc. In one chapter the Laws of Absorption and the Nomenclature of Absorption Spectrophotometry are considered. The well-known formulae for Lambert's Law and Beer's Law are discussed at length, the latter in much detail, with special reference to apparent exceptions; also an "Appendix" is devoted to the Algebraical Expression of Beer's Law. A chapter on Applications of Absorption Spectrophotometry and the Raman Effect opens with an interesting review of the earlier history of the subject, and leads on to a brief study of a few instances of both qualitative and quantitative applications of absorption spectra; the last is exemplified by the admirable work of Campbell Smith on serum proteins. Within the compass of a single page is given a good introduction to the Raman effect.

The later, larger section on "The Technique of Absorption Spectroscopy" deals with the instrumental equipment and with the scientific principles on which the many instruments are constructed. The "Spekker" spectrophotometer, which is usually, although not in this volume, described as the less costly

offspring of an earlier and more elaborate model, takes now the leading place. The "Notched Echelon Cell," introduced in 1932, provides means for obtaining a series of spectra with one or two ml. of solution in half a minute. It gives all that is needed for a first absorption curve. Finally, a new photo-electric photometer is presented, for comparing the intensities of two spectrum lines. This, although primarily intended as an instrument of precision, will come as a great boon to many whose personal observations are uncertain, although others may be able to do trustworthy work without such aid.

The book will be welcomed by every one interested in absorption spectroscopy, whether from the standpoint of theoretical chemistry or from the industrial or other applied aspect. It brings before the reader some of the more remarkable of the many developments of method in a vast field of inquiry, which, in response to the new demands of workers on fresh problems, continues to enlarge its borders with a bewildering persistence.

The volume does credit to the producers; the print is clear and well arranged, while the several plates bring into good evidence the details to be demonstrated.

S. JUDD LEWIS

THE CARBOHYDRATES. By E. F. ARMSTRONG, D.Sc., Ph.D., LL.D., F.R.S., and K. F. ARMSTRONG, M.A., B.Sc. Fifth Edition. Pp. vi+252. London: Longmans, Green & Co. 1934. Price 15s. net.

Since the publication of the fourth edition of Dr. E. F. Armstrong's monograph, "The Simple Carbohydrates and the Glucosides," in 1924 (ANALYST, 1924, **49**, 497), great progress has been made in these branches of organic chemistry, and the work has now been published in two parts, of which one, "The Glycosides," appeared in 1931 (ANALYST, 1932, **57**, 481); the other forms the subject of the present review.

The vast amount of research on the sugars carried out during the past ten years is indicated by the long lists of references appended to each chapter, and the results of some of this research are so fundamental that it has been found necessary to re-write the book completely. Thus, ten years ago, the more stable (α- and β-) form of glucose was supposed to contain the butylene oxide ring structure and the less stable, so-called γ-glucose was supposed to contain the propylene oxide structure. The work of Haworth and his collaborators, however, has shown that the more stable glucose contains an amylene oxide structure and the less stable glucose contains the butylene oxide structure previously ascribed to stable glucose. Haworth has, therefore, designated these forms of glucose as (α- and β-) glucopyranose and (α- and β-) glucofuranose, thus indicating the relations between these sugars and the pyran and furan rings, respectively. Glucose is such an important building material in the carbohydrate edifice, that these new views as to its structure are of very wide significance. The corresponding isomers of fructose are named fructopyranose and fructofuranose and, according to Haworth, sucrose appears to be a compound of α-glucopyranose and fructofuranose. As is pointed out by the authors, however, the condensation of these compounds might give rise to ten different substances, and it is not surprising that sucrose has not yet been synthesised. The far-reaching importance of the new views concerning the

structure of glucose and fructose is shown throughout the book, and especially in Chapter XV, which deals with the structures of the di-, tri- and tetra-saccharides. For this group of carbohydrates the authors have adopted the name "oligosaccharides," proposed by Freudenberg; it deserves to find general acceptance.

A very brief description of the polysaccharides is given in Chapter XVII as a supplement to the account of the simpler carbohydrates which occupies the first sixteen chapters. The two concluding chapters, dealing with the relation between configuration and biological behaviour and with the synthesis of carbohydrates in the plant, will be of special interest to the biochemist.

The earlier editions of this book by Dr. E. F. Armstrong formed extremely valuable epitomes of sugar chemistry and the same may be said of the new edition by Dr. Armstrong and his son; it is a masterly survey of our present knowledge of the subject. By the recent untimely and widely-mourned death of Mr. K. F. Armstrong this field of research has lost a worker of great promise.

LEWIS EYNON

VOLUMETRIC ANALYSIS. By H. P. STARCK, M.A. Pp. 228+31. London: Baillière, Tindall & Cox. 1934. Price 7s. 6d. net.

This is a students' book and is intended primarily to satisfy the requirements of the standard of University Scholarships, although a few pages at the end of each section are devoted to rather more advanced work for Intermediate and Final B.Sc. students. It follows the usual lines of such publications, and indeed, calls for little comment, being well-written and accurate. The author is without doubt best entitled to judge what should be included and what omitted; thus the chapter on *p*H values and the theory of indicators was a wise choice, and is well executed. At the same time, in view of the increasing importance of oxidation-reduction indicators, one would have expected to find some reference to them, especially as the use of diphenylamine is described under its appropriate reaction.

The up-to-date standard of the book is indicated by the inclusion of details for the use of tartrazine as an adsorption indicator, and it is a pity that rhodamine was not substituted here, as it is much better. Potassium iodate is referred to as an oxidising agent, but not as a means of standardising acids (for which it is extremely useful), and the method given for the determination of sulphites in glucose is quite unsatisfactory.

However, the book fulfils extremely well the main purpose for which it is intended, and the problems and answers (for which the author assumes complete responsibility) and appendix, containing the usual tables for qualitative analysis, should afford additional help to the student.

JULIUS GRANT

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