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Deaths.

With great regret we record the deaths of the following members:

H. D. ELKINGTON, July 1st, 1938.

G. N. HUNTLY, August 2nd, 1938.

F. W. TOMS, July 20th, 1938.

Obituary notices will be published later.

Citric Acid Determinations in Milk and Milk Products

BY PAUL S. ARUP, PH.D., F.I.C.

THE PENTABROMOACETONE METHOD (GENERAL).—The results of citric acid determinations recorded here were obtained by the pentabromoacetone method, which is now coming to be generally recognised as the most satisfactory available.

At the outset it was realised that none of the descriptions of the method given in the literature was entirely satisfactory, the best at the time being that of the A.O.A.C.,[1] which allows for the slight solubility of pentabromoacetone in water. The procedure adopted was based on the A.O.A.C. method, but with the important difference that potassium permanganate solution was added slowly, with stirring, to the acidified citric acid solution containing potassium bromide, instead of all at once. The fact that the purity of the pentabromoacetone depends on the care with which the oxidation is carried out, has already been indicated by Lampitt and Rooke,[2] and the matter is only stressed further because it was observed that the impurities in pentabromoacetone, due to rapid oxidation, are largely of such a degree of volatility as to interfere with the drying to a constant weight in a vacuum desiccator, and it is probably this fact which is responsible for difficulties noted that have been ascribed to the supposed volatility of pentabromacetone.[3,4,5] Under proper conditions, any loss of substance during the period of drying which is sufficient to remove moisture will be negligible.

An investigation of the method has been published by Lampitt and Rooke,[2] who have laid down a mode of procedure which may well be adopted as a standard for routine determinations of citric acid in dairy products not containing notable amounts of cane sugar or other readily oxidisable material. It is unnecessary to go further into the details of the method used for the actual determination of citric acid as it was found by comparative analyses that the results were the same as those obtainable by the procedure of Lampitt and Rooke after this had been published, the bulk of the work having been done before. A description may, however, be given of the method of preparation of sweetened condensed milk samples for citric acid determinations, for in the presence of notable amounts of cane sugar the quantitative conversion of citric acid into pentabromoacetone fails; the bromine liberated by the action of the permanganate on the bromide in the acid solution is so rapidly removed from the sphere of action that the conversion of some of the citric acid stops short at the acetone dicarboxylic acid stage, with consequent loss owing to the decomposition of this acid into acetone and carbon dioxide. Attempts to carry out the reaction at room temperature instead of at 45° to 50° C. were equally unsuccessful, the results in all cases being low and erratic. The sugars of malt extract or other similar easily oxidisable materials interfere in the same manner, and the method now described is therefore recommended for the analysis of malted milk and milk chocolate (see page 640).

THE METHOD FOR DETERMINING CITRIC ACID IN SWEETENED CONDENSED MILK, ETC.—After various trials, the following method, depending on the precipitation of the citric acid as the lead salt, was fixed on as being the most satisfactory.

Weigh out 20 g. of the sample in a wide-necked 100-ml. flask (such as the Reichert type), add 60 ml. of hot water, heat on the water-bath and mix thoroughly, add 8 ml. of 50 per cent. trichloroacetic acid, mix and heat on the water-bath for half-an-hour, shaking occasionally. Cool, make up to 100 ml., filter and measure an aliquot portion of the filtrate (usually 75 ml.) into a 100-ml. beaker. Add phenolphthalein and then sufficient sodium hydroxide solution (at first a strong solution and finally $N/10$) to produce a faint pink tint. Add an excess, usually 10 ml., of neutral lead acetate solution (15 per cent.), mix, allow to settle and filter off the precipitate on a Gooch crucible with about 0·1 to 0·2 g. of asbestos; after sucking dry, wash with 10 ml. of water. It is not necessary to remove all traces of sugar or to transfer all traces of the precipitate to the filter. Transfer the crucible with the precipitate and asbestos to the beaker previously used, add 70 ml. of hot water and 15 ml. of 50 per cent. (by vol.) sulphuric acid, stir up the precipitate and asbestos in the acid, warm on the water-bath for 15 minutes with occasional stirring, transfer to a 110-ml. (Reichert) measuring flask, cool, make up to the 110-ml. mark with water, and filter off 100 ml. for the determination of citric acid, which will proceed normally after the treatment just described. As regards volume corrections for the precipitates, it was found that for the first precipitate the formula

$$v = \frac{W}{100} [(1 \cdot 08 \times F) + (1 \cdot 55 \times P)]$$

where v represents volume of precipitate in ml., W weight of sample in g., F percentage of fat in sample, and P percentage of protein (N × 6·38) in sample,

gives sufficiently accurate results. For the second precipitate, with the quantities given, the volume of the lead sulphate and asbestos may be taken as 0·4 ml.

RESULTS OF DETERMINATIONS OF CITRIC ACID IN MILK AND MILK PRODUCTS.—*In Milk.*—The 25 samples analysed were all fresh retail milk of normal composition in good bacteriological condition. The reductase test in every instance showed reduction times of not less than seven hours, and the titratable lactic acid content was 0·13 to 0·15 per cent. The results may therefore be taken as not having been affected by loss of citric acid due to fermentations.

In the following list, which gives the results of the determinations as percentages of anhydrous citric acid by weight, E. and M. stand for evening and morning milks, respectively.

1935—Aug., E. 0·174, M. 0·176; Sept., E. 0·166; Nov., E. 0·169, M. 0·174; Dec., M. 0·195, E. 0·185; E. 0·168, 0·206. 1936—Jan., M. 0·152, E. 0·160; Feb., E. 0·166, M. 0·171; Mar., M. 0·166, E. 0·171, 0·152, 0·155, M. 0·153; May, E. 0·164, 0·151, M. 0·168, 0·150; June, E. 0·159, M. 0·172; Sept., E. 0·165.

The maximum was 0·206, the minimum 0·150, and the average 0·168 per cent. of anhydrous citric acid.

In Condensed Milk.—The sixteen samples of Table I were retail samples of normal composition and quality. The figures in the last column for reconstituted milk were obtained by calculation to a basis of milk with 3·4 per cent. of proteins and 3·5 per cent. of fat.

TABLE I

CONDENSED MILK

Sample No.	Description	Origin	Citric acid (anhydrous) in sample Per Cent. (by weight)	Citric acid (anhydrous) in reconstituted milk Per Cent. (by weight)
1	Full cream, unsweetened ..	English	0·494	0·188
2	,, ,, ,, ..	Irish	0·463	0·185
3	,, ,, ,, ..	New Zealand	0·484	0·179
4	,, ,, ,, ..	,, ,,	0·452	0·177
5	,, ,, ,, ..	English	0·400	0·164
6	Full cream, sweetened ..	Irish	0·506	0·190
7	,, ,, ,, ..	,,	0·473	0·178
8	,, ,, ,, ..	,,	0·468	0·179
9	,, ,, ,, ..	,,	0·458	0·166
10	,, ,, ,, ..	Japanese	0·467	0·205
11	Separated, sweetened ..	Dutch	0·528	0·160
12	,, ,, ..	,,	0·517	0·167
13	,, ,, ..	,,	0·486	0·162
14	,, ,, ..	,,	0·588	0·196
15	,, ,, ..	,,	0·548	0·183
16	,, ,, ..	,,	0·468	0·166
	Average			0·178

Two samples of sweetened condensed milk of Chinese manufacture gave the following figures:

No. 1. Proteins, 11·74; fat, 5·5; citric acid, 0·498 per cent. In reconstituted milk:—fat, 1·60; citric acid, 0·144 per cent.

No. 2. Proteins, 11·80; fat, 7·5; citric acid, 0·364 per cent. In reconstituted milk:—fat, 2·18; citric acid, 0·102 per cent.

These results have not been included in the above table, as the samples were not of good quality, being abnormally brown in colour; No. 2 was worse than No. 1.

The abnormally low citric acid contents are possibly due to the samples having been made from stale milks which had lost some of their citric acid through fermentation; they had evidently been treated drastically in the process of manufacture.

In Sterilised Tinned Cream.—Four samples of Irish manufacture, containing from 22 to 25 per cent. of fat, were examined. In the following list of results showing percentages of anhydrous citric acid by weight, the first figures apply to the cream samples, and the second to the respective results calculated to milk containing 3·5 per cent. of fat.

Sample 1:—0·133, 0·167. Sample 2:—0·166, 0·200.
Sample 3:—0·140, 0·178. Sample 4:—0·144, 0·178.

In Dried Separated Milk.—The results of determinations of citric acid in 11 samples of separated milk powder are given in Table II; of these, the first six were manufactured by the spray process and the last five by the roller process. The citric acid percentages (anhydrous by weight) given in the last column, were calculated to liquid milk (9·0 per cent. of solids not fat and 3·5 per cent. of fat) taking account of the water percentages, which varied from 2·19 to 8·46 per cent.

TABLE II

SEPARATED MILK POWDER

Sample No.	Description	Origin	Citric acid (anhydrous) in powder Per Cent. (by weight)	Citric acid (anhydrous) in reconstituted milk Per Cent. (by weight)
1	Spray process	English	1·64	0·160
2	" "	"	1·72	0·166
3	" "	"	1·86	0·171
4	" "	American	1·81	0·173
5	" "	"	1·62	0·151
6	" "	"	1·72	0·163
7	Roller process	Irish	1·85	0·177
8	" "	"	1·79	0·171
9	" "	"	1·80	0·176
10	" "	"	1·88	0·184
11	" "	"	1·73	0·169
	Average			0·169

EFFECT OF HEAT-TREATMENT ON CITRATES IN MILK.—It was found by Rogina[6] that the citric acid percentage in milk was unaltered by boiling or warming for 15 minutes. To test this point under more stringent conditions, two samples of milk were heated in an autoclave—No. 1 for 15 minutes at 115° C., and No. 2 for 20 minutes at 120° C. No. 1 showed a citric acid content of 0·164 per cent. before and 0·162 per cent. after heating; No. 2 showed 0·170 before and 0·169 per cent. after heating. The effect of heating under these conditions is thus seen to be negligible, and the same may be fairly assumed as regards the heat-treatments applied to milk in the manufacture of the products which have been dealt with above.

DISCUSSION OF THE RESULTS OF CITRIC ACID DETERMINATIONS IN MILK AND MILK PRODUCTS.—The results of citric acid determinations in 25 samples of fresh retail milk obtained locally at intervals over a period of about a year, varied from 0·0150 to 0·206 per cent., showing an average of 0·168 per cent. (p. 637). The averages of the morning and evening samples were practically identical; the number of samples dealt with was, however, not large enough for more detailed comment.

The results of the determinations on condensed milks, tinned creams and milk powders from various parts of the world, when calculated in terms of normal liquid milk, confirm these figures; these samples—31 in all—showed variations from 0·151 to 0·205 per cent. of citric acid when the results were thus re-calculated.

In presenting analytical figures obtained from manufactured products, it is necessary to deal with possible objections that the relative proportions of citric acid to the other non-fatty milk solids may have been in some way altered during the process of manufacture. As regards the effect of heat, this has been dealt with above; it would appear that there is no appreciable effect due to heat-treatment. As regards the possible addition of citrates to condensed milk or tinned cream as a stabiliser, it is understood that this is seldom done, and that phosphates are usually used for purposes of salt balancing where this may be necessary; in any event it would appear that the amounts of citrate that would be added would be very small in proportion to the naturally occurring citrates; thus Sommer and Hart[7] found quantities of the order of 0·001 to 0·002 per cent. to represent the maximum proportions of citrate necessary for producing satisfactory results in condensing.

There remains the possibility of loss of citric acid by the action of micro-organisms, but from the general trend of the results this does not appear to have been a factor of any importance, except with the Chinese samples described above (p. 638).

It would appear that for mixed milk, the estimate of Richmond[8] that "Citric acid is contained in milk to the extent of 0·15 to 0·20 per cent." was a sound one, in spite of the comparatively unsatisfactory methods of determination available at the time. On the other hand, the findings of some more recent investigators must be questioned; Kieferle, Schwaibold and Hackmann[9] found, for mixed retail milk, values some 25 to 30 per cent. higher than those just mentioned, their average value being 0·27 per cent. of citric acid. They used a microcentrifugal method in which the volume of the solid pentabromoacetone was measured; this technique,

although ingenious and apparently capable of giving concordant results, probably suffers from the defect that the capillaries of the micro-centrifuge tubes were calibrated by estimations with solutions of pure citric acid, whereas they were actually used for determinations in milk; slight differences in the physical conditions of the pentabromoacetone produced in the two sets of cases could quite conceivably have caused erroneous results. In fact, experience in the precipitation of pentabromoacetone under various conditions leads to this conclusion. This finding has been referred to in some detail, not only on account of its bearing on the citric acid content of mixed milk but also on account of the interest of microchemical methods to biochemists.

THE DETERMINATIONS OF CITRIC ACID IN VARIOUS FOODS.—In determining citric acid in such materials as malted milk and milk chocolate, the method described above for use with sweetened condensed milk (p. 636) should be used, 20 g. of the sample being taken and treated as directed. The sucrose and the malt extract sugars interfere with the determination when carried out in the ordinary way. Malt extract and chocolate without milk yield only slight traces of "apparent citric acid" in the process, and it was found that estimates of the probable proportion of milk entering into the composition of malted milk or milk chocolate could be made on the basis of citric acid determinations in these materials, though the variations in the natural citric acid content of mixed milk render such estimations only approximate.

Various samples of milk bread and biscuits which had been made with milk were examined and found to contain no citric acid; it is to be presumed that this was due to loss by fermentation; the evidence given above (p. 639) renders it improbable that heat-treatment can have been a factor.

I wish to thank the Department of Agriculture, Dublin, for permission to publish this paper.

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BUTTER TESTING STATION
HARCOURT TERRACE, DUBLIN, S.W.3
March 10th, 1938

A New Iodine Method for the Determination of Starch. Part III

The Determination of Farinaceous Matter in Sausages, Meat Pastes and Fish Pastes, with a Note on their Analysis

BY F. W. EDWARDS, F.I.C., H. R. NANJI, PH.D., D.I.C., F.I.C., AND W. R. CHANMUGAM, F.I.C.

THE method of Stubbs and More[1] for the analysis of sausages has been for a number of years regarded as the standard one, although the actual water-protein ratios to be used in the calculations for different meats were modified by Jackson and Jones.[2] The method was worked out in connection with the Meat Rationing Order of 1918—now obsolete—which required first quality uncooked sausages to contain 67 per cent. of meat and second quality to contain 50 per cent. No standards were laid down for the amount of farinaceous matter, nor was there a definition of "meat" or any suggested limit to the amount of fat that might be present as distinct from lean meat. No direct determination of the amount of starch was made, this constituent being estimated by deducting the total of protein and ash from the non-fatty solids. The "meat" figure was obtained from the amount of nitrogen, and several difficulties were pointed out in the discussion which followed the paper. Some of these were more imaginary than real, and although the determination of the exact amount of meat can never be possible, owing to the natural variations which are fully described by Jackson and Jones (*loc. cit.*), with most ordinary samples it is possible to obtain results that are very near the true value—compare Table III in this communication.

A difficulty that has arisen in recent years is the addition of soya meal to sausages, and it is probable that this use of soya is likely to increase, since sausage mixtures which contain it are characterised by their agreeable softness, improved appearance and keeping qualities, to which may be added the important claim of the soya bean to high food value. The inclusion of soya meal, or any other meal rich in nitrogen, will obviously lead to erroneous results in the calculation of lean meat.

Perhaps the most satisfactory way to standardise these products is to limit the amount of farinaceous matter, water, and possibly fat. It may be of interest to point out that under the Dutch Food Law uncooked sausages may contain only 4 per cent. of starch, and though there is no actual standard for the amount of meat, the percentage composition has to be given on the label. Similarly, in Belgium the only stipulation for sausages is that starch shall not exceed 8 per cent., in the U.S.A. not more than 2 per cent. of cereal matter is permitted, in Canada a limit of 5 per cent. of cereals in addition to a maximum limit of 60 per cent. of water is imposed, and in Australia (certain States), New Zealand and South Africa the standards require sausages to contain 75 per cent. of meat and not more than 6 per cent. of starch.

Regarding the composition of fish and meat pastes, a glance at some of the recipes recently published[3] will show the diverse character of these products. It

is common knowledge that the named fish in a fish paste is often merely the one giving the dominant flavour (*cf.* Cox[4]), with the result that any composition arrived at by analysis is bound to be in the nature of a mere indication; therefore, in dealing with meat and fish pastes the only possible course available, if any standards are adopted in this country, is to impose limits for starch, water and fat. A limit of 5 per cent. of dry starch in fish and meat pastes is general in many countries. In this connection it may be significant to quote a statement[5] that "the amount of rusk present in fish or meat pastes should not exceed 10 per cent. of the total weight, otherwise Public Health Authorities would be likely to take action." This statement is all the more welcome as it comes from the trade and probably represents the considered opinion of good-class manufacturers.

We have worked out a method for the direct determination of starch in meat and fish products which gives consistent and reliable results and is fairly rapid. It is a modification of the gravimetric starch iodide method[6] and the complete details are as follows:

Five g. of the well-mixed sample are weighed directly into a 100-ml. beaker and made into a paste with 5 ml. of 5 per cent. alcoholic potash, a flattened glass rod being used for mixing. Fifty ml. more alcoholic potash are then added and the mixture is heated on a water-bath for 15 minutes. The beaker is then allowed to stand for a few minutes and the supernatant liquid is decanted through filter paper in a Buchner funnel without disturbing the residue. This procedure of adding alcoholic potash, heating and decanting, is repeated twice more. The residue in the beaker is now boiled twice with 80 per cent. alcohol, and the liquid is again decanted through the same filter,* the alcohol being drained as completely as possible the second time. The small amount of residue on the filter is transferred back to the beaker with 0·7 per cent. aqueous potash from a wash-bottle with a fine jet. About 75 ml. of aqueous potash are added with stirring, and the starch is gelatinised by gentle simmering over a gas burner for half-an-hour. The liquid is transferred while hot to a 200-ml. measuring flask, and the beaker is washed further with small quantities of water, after which the mixture is cooled and diluted to 200 ml.

TABLE I

Material	Total starch found g.	Added starch found g.
5 g. of minced meat (for "blank")	nil	—
5 g. " " " with 0·5 g. dry starch ..	0·490	0·490
5 g. " " " with 0·25 g. "	0·261	0·261
5 g. of beef sausage	0·476	—
5 g. " " " with 0·5 g. dry starch ..	0·980	0·504
5 g. " " " with 0·25 g. "	0·733	0·257
5 g. of pork sausage	0·210	—
5 g. " " " with 0·5 g. dry starch ..	0·706	0·496
5 g. " " " with 0·25 g. "	0·470	0·260

An aliquot part (10 to 20 ml. is usually sufficient) of the filtered solution is neutralised to phenolphthalein with dilute acetic acid in a 100-ml. beaker, 1 to 2 ml.

* The total filtrate should be reserved for determination of the fat.

of 0·1 *N* iodine solution is added (excess should be present), followed by 40 ml. of 95 per cent. alcohol, with stirring. After standing for 5 minutes, the liquid is filtered through a tared alundum crucible (medium grade), and the residue is washed with alcohol, dried and weighed.

We have checked this method in two ways. For the first, see Table I.

The second method we employed as a check was to compare the actual amount of starch found in the sample with the figure obtained by deducting ash and protein from the non-fatty solids. The figures in Table II show that there is good agreement in most instances, but that with beef sausages the results do not agree well; we are not at present able to account for this; it may be that some other carbohydrate filler was also present in the particular brands with which we experimented.

TABLE II

Sample	Starch actually found Per Cent.	Non-fatty solids minus ash and protein Per Cent.
Pork sausage 1	3·0	3·8
" " 2	7·1	6·7
" " 3	4·0	4·2
" " 4	8·4	8·8
" " 5	7·1	8·0
Beef sausage 1	12·4	11·7
" " 2	10·0	12·64
" " 3	14·8	20·5
" " 4	18·6	24·3
" " 5	12·4	14·6
Bloater paste 1	4·9	5·9
" " 2	3·5	3·5
" " 3	nil	0·56
" " 4	3·99	4·6
" " 5	7·97	8·24
Wild duck paste	3·1	3·3
Chicken and ham paste 1	3·5	3·6
" " " " 2	6·2	6·24
" " " " 3	4·0	4·3

ANALYSIS OF SAUSAGES, MEAT PASTES AND FISH PASTES.—For the routine examination of these products we determine moisture, starch and fat. The moisture is determined by the usual method and the starch as already described. For the determination of *fat* we collect the alcoholic potash filtrate and alcoholic washings in a 200-ml. measuring flask, make up to bulk with more alcohol, and then proceed as follows:—Twenty-five ml. are diluted, in a separating funnel, with about 100 ml. of water, acidified and extracted with ether three times; the ether is evaporated and the residue is dried and weighed.

$$\text{Wt. of fatty acids} \times 1{\cdot}1 = \text{fat in 25 ml.}$$

This method of determining the fat avoids a separate determination directly on the sample and, moreover, is much less tedious than the method suggested by Stubbs and More of repeated extraction with ether after drying the sample,

which is apt to give low results if the last traces of fat are not removed by exhaustive extraction.

If a complete analysis is required, the only other determinations necessary are those of ash and nitrogen.

In view of the possibility of new food legislation and standards, we have included in Table III complete analyses of some representative products. In calculating lean meat we have used the modified water-protein ratios suggested by Jackson and Jones which, in our experience, give an approximation closer than those of Stubbs and More. It is satisfactory to note that the composition of the average products on the market to-day is quite good, and this is an argument in favour of adopting standards, as such would afford protection not only to consumers, but also to honest traders. It may be remarked that beef sausages, as a rule, contain more farinaceous filler than pork sausages, probably because of the lower fat-content of the former meat.

Taking the figures in Table III as a guide, limits of 7 per cent. of dry starch for pork sausages and 15 per cent. of dry starch for beef sausages would appear to be reasonable. If it is considered desirable to permit two qualities to be sold, it should not be difficult to fix other limits for the second quality.

TABLE III

Sample	Total solids Per Cent.	Fat Per Cent.	Starch Per Cent.	Ash Per Cent.	Total protein Per Cent.	Total meat Per Cent.
Pork sausages 1	46·7	28·6	3·0	2·5	11·8	78·4
" " 2	53·6	34·7	7·1	2·1	10·1	75·1
" " 3	54·5	36·8	4·0	2·2	11·3	84·3
" " 4	49·5	28·0	8·4	2·4	10·3	69·4
" " 5	53·7	33·8	7·1	1·93	9·93	73·4
Beef sausages 1	42·08	18·92	12·4	2·27	9·2	54·3
" " 2	41·7	16·7	10·0	1·76	10·6	58·3
" " 3	50·36	19·36	14·8	1·9	8·55	46·7
" " 4	43·9	9·6	18·6	2·55	6·5	25·4
" " 5	45·3	20·5	12·4	2·2	8·0	49·25
" " 6	50·8	18·5	17·9	2·3	7·7	40·9
Pork sausages (known recipe):						
1. 16·6 per cent. of meat	39·3	2·5	22·6	0·48	7·6	19·8
2. 66·6 " " " "	34·9	7·5	9·75	0·91	14·65	65·75
3. 83·3 " " " "	53·3	26·8	9·3	1·07	13·8	81·8
4. 50·0 " " " "	36·1	5·5	16·84	0·56	11·6	53·3
5. 75·0 " " " "	52·4	33·9	7·1	2·1	10·4	75·7

In giving the analyses of some fish and meat pastes (Table IV), we have made no attempt to arrive at the actual composition of these products, because we do not consider it would serve any useful purpose. What is of most importance is the actual amount of starch present, and, judging by the analyses published by Cox,[4] as well as by our own figures, it would appear that the limit of not more than 5 per cent. of dry starch adopted in some countries is quite a fair one.

TABLE IV

Sample	Total solids Per Cent.	Fat Per Cent.	Starch Per Cent.	Ash Per Cent.	Protein Per Cent.
Bloater paste 1	42·2	13·6	4·9	4·3	18·9
„ „ 2	38·7	12·5	3·55	4·0	18·8
„ „ 3	76·2	45·7	nil	10·2	19·7
„ „ 4	39·8	9·7	3·99	6·93	18·6
„ „ 5	43·25	15·4	7·97	5·05	14·5
Wild duck paste	39·2	13·8	3·1	2·5	19·6
Chicken and ham paste 1	35·2	9·0	3·5	2·1	20·5
„ „ „ „ 2	39·8	12·9	6·2	2·56	18·1
„ „ „ „ 3	38·6	14·2	4·0	3·0	17·1

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ANALYTICAL LABORATORIES
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February 2nd, 1938

The Extraction of Alkaloids and other Organic Drugs from Viscera

BY F. BAMFORD, B.SC.

Two important papers—one by Stewart, Chatterji and Smith[1] and the other by Daubney and Nickolls[2]—have recently been published on this subject. Both papers—the former from Edinburgh University and the latter from the Hendon Metropolitan Police Laboratory—suggest discarding the Stas-Otto process, even in a modified form, and giving up the use of rectified spirit for extraction; both agree in condemning the use of lead salts to purify extracts. My opinion is based on the examination of many hundreds of samples of viscera and excreta during the twelve years 1926 to 1938, and I believe the case for the discarding of alcohol for extraction and of lead salts for purification has still to be proved.

The work in Edinburgh and Hendon is, naturally, incomplete, and many poisonous drugs insoluble in water but soluble in alcohol have still to be considered. Moreover, there is often a difference between the conditions of routine work in a laboratory such as that of the Medico-Legal Department in Egypt (where samples of viscera in varying degrees of putrefaction, the whole mass being sometimes semi-fluid, reach us almost daily) and the conditions in Great Britain. Again, the samples of viscera often reach the laboratory preserved in alcohol, so that

partial extraction of the poison has already occurred before the samples reach the analyst.

A further practical difficulty in following the Hendon technique of freezing the viscera is that one or two refrigerators would be totally inadequate for a department such as ours, and the expense of installing the necessary number might be prohibitive.

The Stas–Otto process is criticised on the ground of slowness. This criticism loses much of its force if certain modifications are introduced. From the alimentary organs I have many times obtained an alkaloid in a satisfactory state of purity within three hours. Usually a complete examination of stomach, intestines (with their contents), liver, kidney, bladder (and contents) takes about four days, with work in the mornings only and with very frequent interruptions.

I agree with Daubney and Nickolls that the extraction of alkaloids from the stomach is usually simpler than extraction from the liver; nevertheless, I have frequently obtained larger and purer extracts from the solid organs than from stomach and intestines, especially when the drug has been injected hypodermically and when death has not occurred until many hours after the ingestion of the poison.

I have been using lead salts regularly for the last seven years, with most satisfactory results, especially in the extraction of strychnine, morphine, solanaceous alkaloids and barbituric acid derivatives. I have also used them with success to purify cocaine and veratrine alkaloids. I have had less personal experience with glycosidal poisons than with alkaloids and, therefore, write of them with less confidence, but the almost universal use of lead salts in the preparation of pure glycosides from plants is significant. In one instance of poisoning by digitaline Nativelle, I used basic lead acetate for the purification of an extract from the solid viscera and obtained a product free from animal matter, giving colour reactions exactly similar to those of an extract made from digitaline Nativelle itself. When injected into a frog the heart of which was exposed the extract caused a diminution of the pulse rate of more than 30 per cent., whilst the heart of a control frog similarly exposed continued to beat steadily. In this connection it is noteworthy that the poison was detected in the solid organs, the patient having lived for two and a half to three hours after swallowing 10 ml. of the solution. According to Peterson, Haines and Webster[3] there is no previous record of the detection of any of the active principles of digitalis in urine, blood or viscera, with the exception of the gastro-intestinal tract.

Some experiments carried out in the winter of 1930–31 established my belief in the utility of the lead process, and seven years' subsequent experience has confirmed it.

The preliminary experiments were carried out with strychnine, atropine and cocaine. Briefly they were as follows:

STRYCHNINE.—An alcoholic extract of animal matter from the slaughter-house, including liver, spleen, stomach and fat, was made. The total volume of two alcoholic extracts and expressed animal fluids from 5 kg. of material was 10 litres. Eight experiments were made, using in general 1 litre of extract and measured volumes of a solution of strychnine sulphate containing 0·5 g. of the base in 100 ml. of water.

The procedure found most satisfactory is illustrated by the following experiment:

One litre of the extract was mixed with 3 ml. of the strychnine solution containing 15 mg. of the alkaloid and evaporated to dryness in an open dish. The residue was taken up with hot acidified water and filtered without suction through a fluted filter-paper (Schleicher and Schüll, No. 572). The residue was washed with hot water and the washings were added to the filtrate. A saturated solution of lead acetate *acidified with acetic acid* was added gradually until precipitation was complete. The lead precipitate was filtered off on a Buchner funnel and washed with hot water. The united filtrate and washings were treated with hydrogen sulphide, and the lead sulphide was filtered off and washed, the washings being again added to the filtrate. The liquid extract was then evaporated to 150 ml., made alkaline and extracted with three portions of chloroform. The total volume of the chloroform extract was 100 ml. One-tenth of a ml. of this chloroform extract (*i.e.* one-thousandth part) yielded on evaporation a residue which gave clear and characteristic colours in the dichromate test.

It is obvious that this method enables one to isolate and identify quantities of strychnine of the order of 0·015 mg. after being mixed with an extract from 500 g. of miscellaneous animal matter, including proteins and fat; in later experiments, in which larger quantities of strychnine were used, the yield of practically pure strychnine base was about 75 per cent.; it was almost colourless, partly crystalline, dissolved in conc. sulphuric acid to a colourless solution, produced a perfect sequence of colours in the dichromate test, and yielded quite characteristic picrate crystals. In a routine case, some time later, the extracted strychnine was further purified by the method hereinafter described (see experiments on cocaine) and obtained chemically pure: m.p. 268° C.

Experiments with Atropine in Urine.—Three experiments were made with the double object of testing the usefulness of lead salts and checking the statements frequently made, that solanaceous alkaloids, being unstable, are peculiarly difficult to extract. I believe that this difficulty, although it exists, is often exaggerated.*

Ten mg. of atropine sulphate (= 8·3 mg. anhydrous alkaloid) were dissolved in 1 litre of urine. Excess of a saturated solution of lead acetate acidified with acetic acid was added, and the precipitate was filtered off and washed. Excess of lead was removed from the filtrate by adding dilute sulphuric acid until the liquid was faintly acid to Congo-red, filtering, washing the lead sulphate with water, and adding the washings to the filtrate. The total volume of the liquid was 1260 ml. This was divided into three equal portions, each corresponding with 3·3 mg. of the original atropine sulphate (2·8 mg. of base).

The first portion was made alkaline with ammonia and extracted three times with chloroform. The residue left on evaporation to dryness gave an unsatisfactory Vitali test. This residue was taken up with acidified water, filtered, and extracted first in acid solution and afterwards in alkaline solution with chloroform. The

* *Cf.* Ipsen–Innsbruck.[4] He claimed to have detected atropine which had been in contact with putrefying organic matter for 12 years, the original quantity of the alkaloid having been 0·03 g.

purified residue, obtained by evaporation of the chloroform extract from alkaline solution, was almost pure white and the Vitali reaction was excellent.

The second portion was made neutral to Congo red (faintly acid to litmus) and evaporated to dryness at room temperature in a dish, evaporation being aided by allowing a current of air to play on the surface of the liquid. The same procedure as in the first experiment again yielded a clean residue giving a definite Vitali reaction.

The third portion was allowed to stand for two weeks. Half of it (corresponding with 1·4 mg. of atropine base) was evaporated as in Expt. 2, but not to dryness, the volume being reduced to 40 ml. This was made alkaline and extracted with chloroform. The dry residue from this extract was taken up in acidified water and treated as before with chloroform first in acid and afterwards in alkaline solution. Again a clean residue giving an excellent Vitali reaction was obtained.

EXPERIMENTS WITH COCAINE IN URINE.—The purity of an extract of cocaine from animal matter is of peculiar importance, since the only satisfactory tests for it are the preparation of good crystals of the auric chloride and the permanganate salts. The presence of animal matter in the extract almost invariably reduces permanganate and inhibits the formation of characteristic crystals.

A stock solution containing 0·56 g. of cocaine hydrochloride (= 0·5 g. of base) in 1 litre of urine was prepared.

Expt. 1.—The urine (100 ml.) containing 50 mg. of cocaine was treated successively with acidified lead acetate solution and dilute sulphuric acid, and the clarified urine was made alkaline and extracted three times with chloroform.

(*Note.*—Extraction in acid solution was omitted. Good crystals of the permanganate were obtained by the use of Hankin's method. The permanganate was reduced very slowly.)

Expt. 2.—This was made on the following day with urine containing a smaller quantity of cocaine (= 5 mg. in 100 ml. of urine). Ten ml. of the stock urine were diluted with 90 ml. of urine free from cocaine. (This urine, by the way, was turbid.) The extract was made in the same way as in Expt. 1. The chloroform extract was not colourless and the residue from it was slightly yellow. A sample of this immediately reduced permanganate. The remainder of the residue was dissolved in water acidified with sulphuric acid and an excess of potassium mercuri-iodide solution (Mayer's reagent) was added. The precipitate was collected on an asbestos filter in a Gooch crucible. The asbestos and precipitate were transferred to a stoppered flask containing an aqueous solution of hydrogen sulphide and shaken for ten minutes. The mixture was then filtered, and the filtrate was made alkaline with ammonia and extracted with chloroform. The residue after evaporation was sufficiently pure to yield excellent permanganate crystals, which were still visible after two hours but had disappeared at the end of four hours, the permanganate being then decomposed.

Expt. 3.—This was carried out after 25 days, the urine having been kept on the laboratory bench in a stoppered bottle. As the urine was very putrid and it seemed reasonable to suspect partial decomposition of the cocaine, an undiluted sample of urine was used for this experiment. One hundred ml. of the original

urine containing 50 mg. of cocaine were treated as in Expt. 2. Excellent crystals were obtained, both with permanganate and with auric chloride.

After this experimental work (*i.e.* since January, 1931), the use of lead acetate has been the standard method in this laboratory whenever alkaloidal poisons or derivatives of barbituric acid have been sought, an acid solution of lead acetate being used for the former and a basic solution for the latter, and I am firmly convinced of its value. Many times I have extracted alkaloids, such as morphine, strychnine and atropine, from liver and other viscera in sufficiently pure condition to yield characteristic crystalline derivatives. Extraction of pure crystalline barbitone (m.p. 194° C.) seldom presents much difficulty.

I agree with the workers in Edinburgh and Hendon that efficient mincing is important, and that this is difficult with an ordinary mincing machine when the viscera are not in a firm condition. My routine procedure is to cut the viscera into small pieces with scissors, make the first alcoholic extraction, and squeeze through muslin. The first part of the squeezing is done by hand. Afterwards a powerful screw-press is used, which converts the residue into a hard cake which can be efficiently minced into a meal-like powder. The alcoholic extraction is repeated twice, leaving a very small residue. The residue from liver and kidneys resembles dry coffee grounds.

The alcoholic extract is, in general, treated as above described, although some modification is occasionally necessary when the animal matter contains much fat. For the removal of the excess of lead salts from the aqueous solution, sulphuretted hydrogen is probably the best method, although sulphuric acid, carefully controlled with Congo red, is much simpler and usually gives satisfactory results.

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MEDICO-LEGAL DEPARTMENT
CAIRO

April 22nd, 1938

Studies in Internal Electrolysis. IV

The Determination of small Quantities of Mercury in the Presence of Copper and Zinc

BY JAMES G. FIFE, M.Sc., F.I.C.

MAY[1] has stated that traces of mercury such as might come from a broken thermometer are sufficient to cause embrittlement of brass condenser tubes. Moore and Beckinsale,[2] in discussing the phenomenon of the "season cracking" of brass, state that in order to test the liability of brass to season cracking it may be pickled in dilute nitric acid and then treated for five minutes with a 1 per cent. solution of mercurous nitrate containing 1 per cent. of nitric acid. Brass which shows cracks after this treatment is liable to the defect of season cracking. A quantitative method of determining mercury in the presence of relatively large amounts of copper and zinc was published by Evans and Clarke.[3] This method was based on complete removal of mercury by deposition on copper and its subsequent determination by sublimation.

TABLE I

No. of experiment	Mercury added g.	Copper added g.	Zinc added g.	Mercury found g.	Time of electrolysis minutes
1	0·0024	5	nil	0·0024	40
2	0·0048	5	nil	0·0048	37
3	0·0073	5	nil	0·0071	40
4	nil	5	nil	nil	36
5	0·0012	5	nil	0·0012	27
6	0·0007	5	nil	0·0007	31
7	0·0048	2·5	2·5	0·0046	33
8	0·0024	2·0	3·0	0·0024	31
9	0·0036	3·0	2·0	0·0035	30
10	0·0060	nil	5·0	0·0059	20

The object of the present investigation was to provide a rapid electrolytic method for the determination of small quantities of mercury in the presence of copper and zinc. It was found that this could be effected by the method of internal electrolysis.

The apparatus employed was that described by Sand,[4] with the modification used in the determination of small proportions of cadmium and of nickel in zinc.[5] The anodes consisted of 18 S.W.G. copper wire.

It was found that satisfactory results could be obtained by using a platinum cathode, an anolyte containing copper sulphate equivalent to 5 g. of copper and 2 ml. of 96 per cent. sulphuric acid per 100 ml., and a catholyte of approximately 300 ml. containing the mercury to be determined (added as nitrate), amounts of copper sulphate or zinc sulphate or both together equivalent to 5 g. of metal, and 6 ml. of 96 per cent. sulphuric acid. The electrolysis was carried out at approximately 60° C. and a time of about 30 to 40 minutes was found sufficient,

but when a new apparatus is set up the time required for solutions of known composition should be determined.

The results are shown in Table I.

Satisfactory results were also obtained by using a platinum cathode but working in a nitric acid solution. In these experiments the anolyte contained copper nitrate equivalent to 5 g. of copper and 2 ml. of conc. nitric acid per 100 ml. and the catholyte (approximately 300 ml.) contained the mercury to be determined (added as nitrate), amounts of copper nitrate or zinc nitrate or both together equivalent to 5 g. of metal and 6 ml. of conc. nitric acid. The electrolysis was again carried out at approximately 60° C.

The results are shown in Table II.

TABLE II

No. of experiment	Mercury added g.	Copper added g.	Zinc added g.	Mercury found g.	Time of electrolysis minutes
11	0·0026	nil	5	0·0026	33
12	nil	2·5	2·5	nil	18
13	0·0048	2·5	2·5	0·0048	30
14	0·0073	3	2	0·0071	26
15	0·0053	3·5	1·5	0·0052	20
16	0·0012	5	nil	0·0012	30

From the results above it will be seen that amounts of mercury ranging from about 0·7 to 7 mg. were successfully determined.

Experiments similar to those described but with the use of a platinum cathode that had been plated first with silver and then with mercury or with silver only, gave less satisfactory results than those described above. The maximum amount of mercury that could so be deposited satisfactorily was about 2 mg. with or without the addition of known amounts of silver.

I wish to thank Dr. Sand for his continued interest in this work.

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The Determination of Unsaponifiable Matter in Whale Oil by the Draft Method of the Norwegian Standards Association

By E. R. BOLTON, F.I.C., M.I.Chem.E., and K. A. WILLIAMS, B.Sc., F.I.C.

The Whale Oil Committee of the Norwegian Standards Association has recently drawn up and published a set of draft standard rules for the testing of whale oil (NS. 489: *Norsk Hvalfangst-Tidende*, 1938, p. 111)* with a possible view to having them agreed as *Tentative Norwegian Standards* and later as International Standards. The draft is claimed to have the approval, on all main points, of the interested German parties through the Deutscher Normenausschuss and to have been based on the Standards and Draft Standards existing in Belgium, Denmark, Germany, Great Britain and the U.S.A., and criticism is invited.

Table I

Comparison of Norwegian and S.P.A. Methods

	Norwegian method	S.P.A. method
Weight of oil taken	10 g.	2 to 2·5 g.
Saponified with	20 ml.	25 ml.
alcoholic potash, strength approx.	3·5 N	0·5 N
The saponified oil is diluted with ..	60 ml. H_2O	50 ml. H_2O
giving a concentration of soap equivalent to g. oil per 100 ml...	12	2·7 to 3·3
This is extracted	at least 3 times	3 times
with ethyl ether, using:		
first time	80 ml.	50 ml.
each subsequent time ..	40 ,,	50 ,,
The extracts are combined and ..	Evaporated; re-saponified with 1 ml. 3·5 N alc. KOH, diluted with 3 ml. H_2O, extracted twice with 10 ml. ether; the extracts are washed 3 times with 10 ml. H_2O, evaporated, dried and weighed.	Washed 3 times with 20 ml. H_2O, then with 20 ml. $N/2$ aq. KOH, 20 ml. H_2O, 20 ml. $N/2$ aq. KOH, 20 ml. H_2O, 20 ml. $N/2$ aq. KOH, 20 ml. H_2O, 20 ml. H_2O; evaporated, dried and weighed.

Amongst the methods of analysis described is one for the determination of unsaponifiable matter, which differs radically from that worked out by the Society of Public Analysts Committee† some years ago.

The latter is now generally accepted in England and has been adopted by the British Standards Institution amongst other authorities. It seemed therefore of

* Published in Norwegian and English by Hvalfangerforeningen (The Association of Whaling Companies), Sandefjord, Norway.

† The method is fully described in the Report of the Sub-Committee on Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soaps to the Standing Committee on Uniformity of Analytical Methods (Analyst, 1933, **58**, 203).

urgent necessity that the Norwegian method should be compared with one so widely used as the Society's and we have accordingly investigated the matter.

The bases of the two methods are set out side by side in Table I, so that a comparison may readily be made. It will of course be understood that we have omitted manipulative details from the table for the sake of brevity and that reference to the original descriptions is necessary for their proper application, but we give sufficient information for the present purpose.

The most important differences between this method and the S.P.A. method lie in:

(1) Extraction from a very much more concentrated soap solution.

(2) The procedure for the removal of soap and unsaponified oil, if present, from the first extracts.

Regarding the second point we may say that as saponification is complete with the first treatment, a second saponification would appear unnecessary. In any case the second saponification introduces far greater possibilities of manipulative errors than the simple washing system of the S.P.A. method.

The first point of difference, however, is of vital importance. Several years ago we proved—in the course of experiments made in this laboratory and reported by us to the S.P.A. Committee, but hitherto unpublished—that three extractions with ether fail to separate the unsaponifiable matter of marine oils completely if the soap concentration exceeds the equivalent of 4 g. of oil per 100 ml. Table II, taken from our original report and dealing with a coast cod oil, clearly illustrates this:

TABLE II

Expt.	Weight of oil used g.	Weight of oil (saponified) per 100 ml. of soap solution g.	Unsaponifiable matter recovered Per Cent.
1	0·5132	0·69	4·72
2	1·2586	1·68	4·74
3	2·0738	2·77	4·73
4	2·1062	2·81	4·75
5	2·5562	3·41	4·72
6	2·5628	3·42	4·70
7	3·3426	4·46	4·68
8	4·9986	6·67	4·31
9	5·0230	6·70	4·29
10	5·5120	7·36	4·06

In these experiments the volumes of alcoholic potash and water used were maintained at 25 ml. and 50 ml., the potash being of sufficient strength to ensure complete saponification.

Two further extractions in Expts. 8 and 9 raised the amount of unsaponifiable matter recovered to 4·73 and 4·72 per cent. respectively. The extracts tested were found to be free from unsaponified oil.

With this information before us we expected to find that the Norwegian method, applied with three ether extractions in the first stage would fail to extract all the unsaponifiable matter and would lead to low results.

This expectation was fully realised on trial. Working with whale oils of this year's catch we have obtained the comparative figures in Table III.

TABLE III

Sample		Unsaponifiable matter extracted, per cent.	
		Norwegian method	S.P.A. method
A	.. ..	1·20	1·72
B	.. ..	0·92	1·53
C	.. 1st test ..	0·93	1·47
	2nd ,, ..	0·91	
D	.. ..	0·84	1·28

Knowing that the material recovered by the S.P.A. method is free from unsaponified oil and soaps and all but traces of free fatty acids, we concluded that the extracted soap solutions remaining at the end of the Norwegian test must still contain a considerable proportion of unsaponifiable matter.

We therefore took the extracted soap solutions from sample A (Table III above) and extracted them four times more with ether, evaporating the extracts and re-saponifying, re-extracting with ether, washing and evaporating under the conditions of the Norwegian method. The results obtained are shown in Table IV.

TABLE IV

TOTAL UNSAPONIFIABLE MATTER RECOVERED

	Per Cent.
Norwegian method:	
3 ether extractions in 1st stage	1·20
5 ,, ,, ,, ,, ,, ...	1·42
7 ,, ,, ,, ,, ,, ...	1·55
S.P.A. method	1·72

It is therefore clear that extension of the extraction procedure from the specified minimum of three extractions to seven fails to secure complete extraction.

To prove that the full remainder of unsaponifiable matter is actually present in the soap solutions remaining after three ether extractions in the first stage, we diluted that from sample C (1st test) with the necessary volumes of alcohol and water to bring the concentrations of soap, alcohol and water to those of the S.P.A. method and carried out the full S.P.A. extraction and washing procedure thereon.

In this way we found the original extract of 0·93 per cent. to be augmented by a further 0·52 per cent., and it will be noticed that these two figures together add to 1·45 per cent., comparing favourably with the 1·47 per cent. obtained directly by the S.P.A. method.

The two extracts of 0·93 per cent. and 0·52 per cent. were combined and the mixture was found to be free from unsaponified oil.

We therefore conclude that the Norwegian method is unsatisfactory, in that it fails to extract all the unsaponifiable matter, and in fact may recover only about 60 per cent. of the full amount. Further, the description allows sufficient variation in the use of the method to render it possible for different workers, applying it according to instructions, to obtain quite different results.

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August 25th, 1938

Erratum: THE DETERMINATION OF ALUMINIUM IN CAST IRON.—In the formula on page 584 (August issue), *for* "0·605 g. of NH_4OH" *read* "0·605 g. of NH_3."

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.

THE DETERMINATION OF NITRITE IN WATERS

THE method usually employed for the determination of nitrite in water is that originally proposed by Griess, using sulphanilic acid and α-naphthylamine in acid solution, and modified by Ilosvay by the substitution of acetic acid for mineral acid. When acetic acid is used the velocity of diazotization is appreciably affected by variation in temperature, decreasing rapidly at low temperatures. Standardised solutions of fuchsin or special standards of tinted glass are frequently used as permanent colour standards, and their use may therefore lead to appreciable error if the determination is not carried out at a definite temperature.

TABLE COMPARING THE EFFECT OF TEMPERATURE ON THE PROPOSED METHOD AND THE GRIESS–ILOSVAY METHOD

(Parts of nitrogen per 100,000)

Temperature ° C.	Nitrite added	Nitrite found (a) By proposed method	(b) By Griess–Ilosvay method
20	0·0012	0·0013	0·0012
15	0·0012	0·0013	0·0010
10	0·0012	0·0012	0·0008
5	0·0012	0·0011	0·0004
20	0·0005	0·0005	0·0005
15	0·0005	0·0005	0·0002
10	0·0005	0·0005	0·0002
5	0·0005	0·0004	less than 0·0001

In the method given below an attempt is made to reduce the effect of temperature by increasing the velocity of diazotization at low temperatures. The sulphanilic acid and α-naphthylamine are added in solution in dilute (1 in 4) sulphuric acid, the strongly acid condition favouring diazotization. Coupling occurs very little at this stage, but is promoted later by adding sodium acetate in slight excess of that required to convert all the sulphuric acid to acetic acid. The reagents are prepared as follows:

SULPHANILIC ACID-α-NAPHTHYLAMINE SOLUTION.—Twenty-five ml. of pure sulphuric acid (sp.gr. 1·85) are added to 25 ml. of water, a drop of bromine water is added to destroy nitrous acid and the excess bromine is boiled off. α-Naphthylamine (0·1 g.) is dissolved in the warm acid and the solution is allowed to cool; 0·8 g. of sulphanilic acid is dissolved in 40 ml. of water and the cold solution of α-naphthylamine is added. When cold, the mixture is made up to 100 ml. with water. This solution keeps well.

AQUEOUS SOLUTION OF SODIUM ACETATE.—Hydrated sodium acetate, $CH_3COONa,3H_2O$ (145 g.) is dissolved in water to give nearly 250 ml. To remove

any nitrite present the solution is heated to boiling, two or three drops of strong titanous sulphate solution are added and boiling is continued until the violet colour disappears. The solution is cooled, filtered and made up to exactly 250 ml. with water.

METHOD.—To 50 ml. of the sample, in a Nessler glass, add 2 ml. of the sulphanilic acid and α-naphthylamine reagent, and after about 10 minutes (15 minutes if the temperature is below 10° C.) add 5 ml. of the sodium acetate solution. The colour develops immediately on adding the acetate solution and the comparison may be made after two minutes.

In the table (p. 655) the proposed method is compared with that modification of the Griess–Ilosvay method which uses reagents that are 4 *N* with respect to acetic acid and matches the colour produced after standing for 15 minutes. The same set of tinted glass standards was used for both methods.

I wish to thank Dr. J. J. Fox, the Government Chemist, for permission to publish this note.

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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.

WATERED MILK

AT the Hull City Police Court, on July, 21st 1938, before Mr. J. R. Macdonald, Stipendiary Magistrate, a farmer of Sutton was summoned by the Corporation under the Food and Drugs (Adulteration) Act, 1928, for selling milk which was found to contain 9·6 per cent. of added water.

Mr. Harrison, for the prosecution, explained that a sample of milk was taken by the Corporation officers in course of delivery from the farm to a retailer. As this milk was found to contain added water, the Corporation Sampling Officer visited the farm on the day following the discovery of the watered sample and took six samples from the cows. Of these "appeal-to-cow" samples, five were of good quality, but the remaining one showed the presence of about 8 per cent. of extraneous water. Owing to the large number of cows at the farm, adequate supervision of the milking was difficult, and so the next day a further six samples of milk were taken from this herd, but before the milk passed over the cooler. The results obtained on these six samples were satisfactory. Twelve samples of milk taken from individual cows a few days later gave normal results on analysis. At the hearing of the case the City Analyst (Mr. A. R. Tankard, F.I.C.) gave details of his analysis. He stated that, owing to the surprising result obtained with one "appeal-to-cow" sample, he had made a very complete analysis and found this milk to contain: fat, 3·8; non-fatty solids, 8·1; ash, 0·69; nitrogen, 0·46; lactose, 4·5; chlorine, 0·078 per cent. The ratio of lactose: protein: ash was not abnormal, the acidity expressed as lactic acid was 0·14 per cent., and the freezing point (Hortvet) was −0·499° C. All these figures showed, in his opinion, that the sample was not a milk of abnormal composition, but a milk containing extraneous water. Corporation water was supplied to the defendant's farm and it contained nitrates to such an extent that 5 per cent. of it in milk could be detected. This "appeal-to-cow" sample gave a definite reaction for nitrates, whilst the control sample of milk from defendant's farm showed no nitrates. On these findings the City

Analyst stated that, in his opinion, the milk was undoubtedly watered. With the exception of the sample mentioned, all the bulk "appeal-to-cow" samples had freezing points (Hortvet) ranging from —0·543° to —0·552° C., and the samples from the twelve individual cows from —0·534° to —0·560° C.

After witnesses for the defence had been heard the magistrate stated that there was no evidence that water had been added wickedly, and he was of opinion that this was not a case for a severe penalty; though he accepted the expert evidence that water was present in the milk, there was nothing to show how it came there. He fined the defendant £3 11s. 6d., including costs.

Notes from the Reports of Public Analysts

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

COUNTY OF DERBYSHIRE

ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1937

Of the 1983 samples of food and drugs examined, 1099 were bought informally.

LEAD IN BEER.—In a case of chronic lead poisoning reported during the earlier part of the year it was found that the patient worked at one hotel and frequented another. Samples drawn at "opening time" at one of these hotels were heavily contaminated with lead, the proportion in one sample being 13 parts per million. In view of these findings, 28 further samples of draught beer were obtained and tested for lead. Of three samples taken direct from the barrel for comparison purposes, two were free from lead and the third contained not more than 0·05 p.p.m. The remaining 25 were obtained well after "opening time" and were thus fairly representative of beer that would have been sold to any customer. Ten samples contained from 0 to 0·19; 2 from 0·2 to 0·29; 7 from 0·3 to 1·4; 6 contained 1·5 p.p.m. or more. The largest amount (5·8 p.p.m.) was found in a sample of bitter beer. These figures undoubtedly indicated that the pipe lines were in a most unsatisfactory condition and a potential danger to health. Proceedings were instituted in respect of certain samples, but it soon became evident that the problem would have to be dealt with in a more comprehensive manner. A circular letter was therefore sent to the licencees and the brewery companies emphasising the point that the analytical results were viewed with concern, and calling for immediate action. R. W. SUTTON

CITY OF PORTSMOUTH

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1937

ICE-CREAM.—Unless some standard is adopted it is feared that, owing to the competition between ice-cream manufacturers, the substitution of other fats for butter-fat will become general. One sample containing vegetable fat was bacteriologically unsatisfactory, containing 800,000 bacteria per 1 ml., and *B. coli* in 0·001 ml. The following results were obtained with samples of ice-cream of different types. Samples Nos. 1 to 6 represented ice-cream made in large plants from milk powder, sugar, fat and water and were all satisfactory from the bacteriological point of view. No. 6 contained vegetable fat. Samples Nos. 7 to 11 were of products made by dairies from milk and cream and were quite unsatisfactory.

Samples Nos. 12 to 16 represented ice-cream made from milk which had been made into custard by boiling with cornflour and then freezing. With the possible exception of No. 16, none of these samples would pass any reasonable standard for bacteriological purity, and this is the more regrettable because at some stage of its preparation the product should have been boiled.

Sample No.	Date	Fat Per Cent.	Total solids Per Cent.	Mineral matter Per Cent.	Bacteria growing on Agar in 1 ml.	*B. coli* Present in ml.	*B. coli* Not present in ml.
Made by ice-cream manufacturers							
1	May 19th	13·8	37·9	0·86	30,000	0·1	0·01
2	May 19th	6·8	34·1	0·74	44,500	0·001	—
3	May 26th	9·0	35·4	1·3	9,000	—	0·1
4	May 26th	10·0	38·7	0·75	4,000	—	0·1
5	August 19th	10·4	39·2	0·86	7,000	0·1	0·01
6	May 26th	11·1	35·4	0·85	1,000	—	0·1
Made by dairies							
7	June 28th	7·3	33·1	0·85	800,000	0·001	—
8	August 12th	8·7	31·9	0·63	Uncountable	0·01	0·001
9	August 12th	31·7	42·3	0·53	1,680,000	0·001	—
10	August 16th	10·4	34·9	0·98	2,000,000	0·001	—
11	August 16th	16·2	38·6	0·77	40,000	0·001	—
Frozen custard							
12	June 28th	2·4	27·1	0·65	1,750,000	—	0·1
13	June 28th	2·5	28·9	0·7	Uncountable	—	0·1
14	August 12th	6·9	33·0	0·74	350,000	0·001	—
15	August 16th	3·4	28·4	0·62	Uncountable	0·001	—
16	May 19th	3·0	26·3	0·66	5,000	0·01	0·001

R. P. PAGE

Department of Scientific and Industrial Research

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY*

II. HYDROGEN CYANIDE VAPOUR

THIS is the second of a series of leaflets describing standard methods for the detection of toxic gases in industry. Leaflet No. 1 (*cf.* ANALYST, 1937, **62**, 607) was concerned with hydrogen sulphide. Apart from its principal use in the fumigation of ships and buildings, hydrogen cyanide is used to a small extent as a reagent in industry, and is encountered in concentrations that may be dangerous in certain industrial processes—in blast furnace plants, dyestuffs works, gas works and coke ovens and in the industries of gold mining and gilding.

POISONOUS EFFECTS.—Hydrogen cyanide acts by stopping the oxidation of protoplasm in the tissue cells. With high concentrations the symptoms appear rapidly—giddiness, headache, unconsciousness and convulsions with cessation of respiration due to paralysis of the respiratory centre in the brain. With weaker concentrations there may be the following symptoms:—Irritation of the throat, palpitation, difficulty in breathing, watering of the eyes, salivation, headache, weakness of the arms and legs, giddiness—followed by collapse and convulsions.

* Leaflet No. 2, H.M. Stationery Office, July 21st, 1938. Price 5s. 6d. net.

The following table shows the effects produced by different concentrations of hydrogen cyanide vapour:—

Parts per vol. (approx.)		Mg. per litre (approx.)	Effects
1 in 50,000	..	0·025	Slight symptoms after several hours.
1 in 10,000	..	0·12	Very dangerous within one hour.
1 in 500	..	2·5	Fatal.

In addition to the danger of inhalation, there is a further danger that the vapours may be absorbed by the skin, especially if the skin is wet with sweat.

METHODS OF DETECTION.—The most important of the various tests that have been described for the detection of small quantities of hydrogen cyanide were examined. Of these tests, the Prussian blue and thiocyanate reactions, which are specific for hydrogen cyanide, are not sufficiently sensitive. The picrate test is neither specific nor sufficiently sensitive. The Congo red and silver nitrate paper test is sensitive but is affected by acid or alkaline gases. Tests depending upon oxidation of the reagent are unsuitable. The Congo red and silver nitrate test and the benzidine and copper acetate reaction, both applied as test-papers, were considered the most suitable and have been developed as quantitative standard tests.

DETAILS OF THE TESTS.—Samples must be taken at a point closely adjacent to the workers, and if there is any chance of the concentration rising, sampling must be done at intervals during the work.

Apparatus.—For sampling the air, a hand exhausting pump, with a barrel of approximately 1·25 in. bore and a capacity of 126 ml., is to be used. The inlet end of the pump shall be screened internally to take a spigot screwed $\frac{7}{16}$ in. Whit., 14 T.P.I. on 0·437 in. diameter. The pump may be fitted with a device for counting the number of strokes. The air sample shall be drawn through a test-paper clamped in a holder of specified design.

TEST-PAPERS.—*Benzidine and Copper Acetate Test.*—(i) Two to 3 g. of pure benzidine acetate are heated in 100 ml. of water for 10 to 15 minutes at 80° C. with constant shaking. When cold, the mixture (which will contain about 1 per cent. of benzidine acetate) is filtered by suction. (ii) Three g. of cupric acetate (of reagent quality) are dissolved in 100 ml. of water. (iii) Immediately before the test is made 25 ml. of solution (i) and 2 ml. of solution (ii) are mixed and stirred well. The mixed reagent will not keep more than 15 minutes. The test-papers are prepared from Postlip No. 633 extra thick white filter-paper cut into strips 2 inches wide. They are immersed in the reagent for 1 minute, drained and allowed to dry in a warm atmosphere. One inch at the top and bottom of the strip is cut off and discarded, and the remainder is cut into 3-in. lengths. The papers must be used immediately.

Congo Red and Silver Nitrate Test.—(i) One g. of pure Congo red is dissolved in 100 ml. of distilled water, and 5 ml. of the solution are diluted to 100 ml. (ii) Five g. of silver nitrate (of reagent quality) are dissolved in 100 ml. of water. The strips of paper are immersed for 1 minute in solution (i) and thoroughly dried, after which they are immersed in (ii) and again dried as rapidly as possible, and away from a strong light, Fresh papers must be made each time a test is required.

Method.—For either test the test-paper is inserted in a special holder (illustrated in the leaflet), and the apparatus is tested for leaks by a technique described in detail. A preliminary indication of the condition of the atmosphere is obtained by making *eight* slow and steady strokes with the pump. The paper is then removed and any stain is compared with the stains on the standard charts provided with the leaflet. In this way an estimate may be made of any concentration between 1 part in 10,000 and 1 part in 20,000 of air by volume, the latter being the maximum that can be inhaled for 1 hour without serious disturbance. If the stain indicates a concentration greater than 1 part in 20,000 a fresh paper is

placed in the holder, and further tests are made with 1, 2, 3 or 5 strokes of the pump; or if a concentration of less than 1 in 100,000 is indicated, a rough estimate of the concentration may be obtained by repeating the test with a greater number of strokes of the pump, until a stain equal to one of the standards is obtained. Comparison of the stains should be made in diffused daylight or with the use of a daylight lamp.

FIRST AID.—The patient should be removed into the fresh air and wrapped in a blanket to keep him warm. If breathing is weak, artificial respiration should be started at once and continued for hours, even after it may seem to have failed. Full details of the treatment of cases of gassing by cyanides are given in Factory Form No. 395 (H.M. Stationery Office, price 1d. net).

RANCIDITY IN EDIBLE FATS*

THIS Report summarises the current state of knowledge concerning the development of rancidity in edible fats and foods containing fats. The scientific aspects of the problem are mainly discussed, but working details of methods likely to be of use in detecting rancidity or correcting faults due to that cause are also given.

The Report is divided into the following parts:—I, The Chemistry of Fats; II, Rancidity: Occurrence and Types; III, The Lesser Causes of Rancidity; IV, The Action of Micro-Organisms on Fats; V, The Deterioration of Fats by Atmospheric Oxidation; VI, Rancidity in Dairy-Products and in the Fat of Meat.

Part V is sub-divided into the following sections:—(i) The Oxidation of Fats; (ii) The Detection and Estimation of Oxidative Rancidity; (iii) The Relation between the Chemical Tests and Rancidity; (iv) Measurement of the Susceptibility of Fats and Oils to Oxidation; (v) The Mechanism of Autoxidation; (vi) Factors which Influence the Rate of Oxidation; (vii) The Stabilisation of Fats by Hydrogenation; (viii) The Yellowing of Fats and Oils; (ix) "Fishiness" in Fat-Containing Foods.

Tables of references to the original papers cited are given at the end of each part and there is a full index.

Connecticut Agricultural Experiment Station

REPORT ON FOOD AND DRUG PRODUCTS FOR 1936

THIS Report summarises the work for 1936, including samples submitted by the Dairy and Food Commissioner and those taken by the Station agent or submitted by health departments and others. Inspection and analysis of feeding stuffs, fertilisers and insecticides also fall within the scope of the work of the department. In 1935 food and drug control was enlarged to include regular biological tests of vitamin D milk and is still in operation.

VITAMIN D MILK.—Milk fortified with vitamin D has become a commodity of considerable importance and there are more than 40 producers of it in the State of Connecticut.

In June, 1935, the Milk Regulation Board officially recognised vitamin D milk and called upon the Dairy and Food Commissioner to undertake inspection and assays of the product as a regular control project. The plan of control is the same as that in effect for other types of market milk and for foods generally. It is done at public expense with funds appropriated for food control and the technical service is rendered by this Station.

* *Food Investigation.* Special Report, No. 46. By C. H. Lea, B.Sc., Ph.D. Pp. 230. H.M. Stationery Office. 1938. Price 3s. 6d. net.

Biological tests such as are necessary to check the units of vitamin D claimed are tedious and frequent tests of the product from a given source are not possible. The effectiveness of the control lies in the fact that the product of any producer may be sampled and assayed at any time. Vitamin D milk marketed in Connecticut is produced by one of three processes: By irradiation, by addition of cod-liver oil concentrate, or by yeast feeding.

During 1936, the period covered by the Report, 62 samples were tested. Of these, 49 were satisfactory and 6 others passable. Seven of the samples produced by yeast feeding were below standard. Results of tests are reported by the Commissioner to the producers and licensers of the several processes, and fresh tests are made to make certain that corrective measures have been taken and that the results are satisfactory.

DETERMINATION OF LACTOSE IN THE PRESENCE OF DEXTROSE IN FRANKFURT SAUSAGES.—A procedure that has given very satisfactory results with the amounts of lactose and dextrose found in Frankfurt sausages is an adaptation of the work of Somogyi (*J. Biol. Chem.*, 1927, **75**, 33), Raymond and Blanco (*ibid.*, 1928, **79**, 649) and Jones (*J. Dairy Res.*, 1936, 7).

Weigh 12·5 g. of the sample into a 250-ml. beaker, add 100 ml. of water, mix thoroughly and boil for 5 minutes. Pour off the extract through a paper pulp mat in a Buchner funnel, using suction. Again boil the residue of the meat in a beaker with 50 ml. of water and pour off as before. Wash the residue twice with approximately 40-ml. portions of boiling water. Combine the extracts in a 250-ml. flask, add 5 ml. of 20 per cent. phosphotungstic acid and cool. Add 2 ml. of hydrochloric acid, dilute to the mark, mix, and filter through a dry paper. Neutralise 200 ml. of the filtrate with sodium hydroxide solution and dilute to 250 ml. (solution A). Use a 50-ml. aliquot part (2 g. of meat) for the determination of total reducing sugars (Munson and Walker).

To Remove Dextrose.—Place 10 ml. of a 25 per cent. suspension of washed Fleischmann's yeast* in a 100-ml. tube and centrifuge. Pour off the water and dry the walls of the tube with filter-paper. Add about 60 ml. of solution A to the yeast in the tube, mix thoroughly, and leave for 15 minutes, stirring frequently enough to keep the yeast in suspension. (Our determinations stood for one hour but it appears that 15 minutes is sufficient.) Again centrifuge, pour off the supernatant liquid through a small, dry filter and determine copper reduction on a 50-ml. aliquot portion.

The difference between the two reductions is due to adsorbable sugar (dextrose); the reduction after yeast treatment is due to lactose.

ORANGEADE.—Regulations in this and some other States provide that the orange juice content shall not be less than 15 per cent.

In October, 1936, the United States Department of Agriculture issued a tentative definition and standard for orangeade, which provides that the orange juice content shall not be less than 25 per cent., and recognises that the acidity of the product may be enhanced by the addition of lemon juice. Until this tentative proposal is affirmed we continue to judge market products on the basis of the minimum of 15 per cent. above mentioned.

We have used the ash-content of orange beverages as a basis of forming an approximate estimate of the proportion of juice present, although it has been suggested that the P_2O_5 content is a better index. In a limited number of trials orange juice prepared in the laboratory at various times from market oranges has shown ash very close to 0·4 g. per 100 ml. of juice. Figures reported to us by a control chemist in a neighbouring State are of about the same magnitude—0·36 to 0·45 g. per 100 ml. The P_2O_5 may be expected to constitute from 10 to 15 per cent. of the ash.

The vitamin content of orangeades is generally stressed in advertising. Vitamin C in fresh orange juice appears to be in the range of 0·4 mg. to 0·6 mg. per ml. and is influenced by variety and probably also by soil conditions. Two samples of laboratory-pressed juices gave values of 0·51 mg. per ml. Conditions

* Wash yeast five times with three times its volume of water, centrifuging each time. The last washing should be clear. Make up a 25 per cent. suspension and keep at 0 to 4° C. Prepare 24 hours before using, and make a blank determination of copper reduction when used.

that favour oxidation result in a diminution of vitamin C. Orangeades prepared from orange concentrates suffer rapid losses of vitamin C at 75° F. and notable losses even at 40° F. (Mack, Fellers, Maclinn and Bean, *Food Research*, 1936, **1**, 223), judged by titration methods.

During the year several samples of orange products have been examined. The results are summarised in the following table, together with results for similar products examined last year. One sample of lemon juice, prepared in the laboratory from fresh lemons, is included.

ANALYSES OF ORANGE PRODUCTS

Product	Ash per 100 ml. g.	P_2O_5 per 100 ml. g.	Vitamin C per ml. mg.	Estimated orange juice content (basis of ash) Per Cent.
1. Orangeade	0·051	0·003	—	13
2. „	0·045	0·005	0·008	11
3. Orange (concentrated) ..	0·243	—	0·228	—
4. „ beverage base ..	1·06	0·112	0·77	—
5. Compound orange dairy base	1·03	0·103	0·77	—
6. 100% pure orange juice ..	0·404	0·041	0·33	100
7. Concentrate..	0·373	—	0·289	—
8. Beverage made from 7 ..	0·048	—	0·015	12
9. Orangeade	0·064	—	0·019	16
10. Concentrate..	0·409	—	0·390	—
11. Beverage made from 10 ..	0·074	—	0·045	18
12. Orange juice, canned ..	—	—	0·450	—
13. „ „ fresh ..	0·41	—	0·510	—
14. „ „ „ ..	0·41	—	0·510	—
15. Lemon juice, fresh	0·26	0·018	0·48	—
16. Orange juice, canned ..	0·41	—	0·42	100

Samples 1 and 2 had 6 and 9·6 per cent., respectively, of P_2O_5 in the ash. On the basis of P_2O_5-content the former would indicate only about 6 per cent. of juice and the latter about 9 per cent.—fair agreement in one instance but not in the other. In No. 6 both ash and P_2O_5 would indicate undiluted juice. Nos. 4 and 5 represent concentrates about 2·5 times that of the original juice. Directions require that sugar should be added. Sample No. 3 was a syrup requiring only dilution with water for beverage purposes. The samples showed loss of vitamin C in varying degrees; in some instances the loss was pronounced.

"TENDRA."—A PREPARATION FOR TREATMENT OF MEAT.—This is a liquid intended to be used in the kitchen to make tough meat more tender and palatable. It is not meant to be applied to meat as offered for sale. From the advertising literature the preparation is, or contains, a vegetable extract that acts upon meat tissue. The papaya fruit, from which *Tendra* is derived, contains papain, and it is said that the Indians wrapped meats in the fresh leaves of this plant to make it more tender. The enzymic activity of *Tendra* was tested by the procedure of Balls, Swenson and Stewart (*J.A.O.A.C.*, 1935, **18**, 140), and for comparison the expressed juice of a fresh pineapple (containing the enzyme brometin) was also examined. The samples were assayed with and without activation by treatment with an equal volume of saturated hydrogen sulphide water. The results were expressed as mg. of the sample necessary to contain one papain unit (*i.e.* that amount of enzymic activity which, by the assay method employed, would produce sufficient acidity to neutralise 1 ml. of N/10 alkali). The sample of fresh pineapple juice, unactivated, was evaluated at from 9000 to 10,000 mg. per papain unit, whilst the corresponding value for the activated juice was about four times as

great—2300 mg. per unit. The sample of *Tendra* without activation showed no pronounced activity, but the activated liquid showed enzymic activity of 800 to 900 mg. per papain unit, or about three times that found for activated pineapple juice. Activation of enzymes may be accomplished in a variety of ways; numerous organic and inorganic substances serve that purpose. Hence it may be that the activity of *Tendra* is initiated or enhanced by substances contained in the meats to which it is applied.

FLUID EXTRACT OF ERGOT.—Twenty-three samples of fluid extract of ergot were examined by the A.O.A.C. colorimetric chemical method of assay. The official test for this preparation is the biological method outlined in the U.S. Pharmacopoeia. This test evaluates the biologically active alkaloids of ergot whereas the chemical method measures the total alkaloids, active as well as inert. Quite recently a new alkaloid has been isolated from ergot and it has been demonstrated that the characteristic biological effects of fluid extracts of this drug are largely due to this new constituent rather than to the alkaloids formerly known. The present chemical method appears to need revision in order to evaluate ergot preparations more closely in terms of the active constituent.

Of the 23 samples examined, 4 contained less than 0·1 mg. per ml. of ergot alkaloids expressed as ergotoxine ethanesulphonate, and 11 contained less than 0·3 mg. per ml. The range found was 0·04 to 0·66 mg. per ml. Where dates of manufacture were available it was found that the low values were identified with old stock. Through the co-operation of one of the pharmaceutical firms interested, tests were made of three of the samples by the U.S.P. biological method, thus affording some comparison with the tests by the chemical method. Both assays were made within an interval of approximately one month.

The comparison is as follows:

	Ergotoxine ethanesulphonate	
No.	By U.S.P. method mg. per ml.	By A.O.A.C. method mg. per ml.
1	0·18	0·33
2	0·33	0·54
3	0·12 (less than)	0·06

The U.S.P. standard for fluid extract of ergot is a potency equivalent to not less than 0·5 mg. of ergotoxine ethanesulphonate per ml. of extract. With due allowance for the difference between the two methods of assay, there is sufficient parallelism to permit of conclusions as to the strength of samples examined. It is evident that a product of minimum U.S.P. potency should be assessed considerably above that minimum when assayed by the present chemical method and that many of the samples examined were sub-standard and some quite inert. The reason for this is, no doubt, largely or entirely due to deterioration from long standing on the druggists' shelves.

British Standards Institution

The following Standard Specification has been issued:

No. 797—1938. ONE-MARK CAPILLARY PIPETTES.

Six sizes of British Standard one-mark capillary pipettes are provided, namely, 0·005 ml., 0·01 ml., 0·02 ml., 0·05 ml., 0·1 ml. and 0·2 ml. Each pipette conforms with the dimensions specified in a table. Internally the bore of the tube is expanded into a chamber at the top of the pipette, and externally the tube is slightly tapered to facilitate the attachment of a rubber tube. The jets of pipettes of nominal capacity 0·005 to 0·05 ml. are tapered externally to a blunt tip with an orifice not exceeding 1·5 mm. for the two smaller sizes and 2·0 mm. for the two larger sizes. On pipettes of 0·1 and 0·2 ml. the jet has a gradual taper and the internal diameter at the orifice of the jet must fall within the limits 0·5 and 1·0 mm. for 0·1 ml. pipettes and 0·7 to 1·2 mm. for 0·2 ml. pipettes. To facilitate identification of pipettes of closely similar dimensions each pipette is marked with an indelible spot of coloured enamel. The tolerances on capacity range from $\pm$0·0004 ml. for 0·005 ml. pipettes to $\pm$0·004 ml. for 0·2 ml. pipettes.

DRAFT SPECIFICATION IN COURSE OF PREPARATION.

A limited number of copies of the following Draft Specification, for the purpose of technical comment, are available to specially interested members of this Society, who should apply directly (mentioning their membership of this Society) and send their comments directly to the British Standards Institution, 28 Victoria Street, S.W.1.

CE (C) 8947. DRAFT B.S.S. FOR COATED TINFOIL FOR USE IN THE DAIRYING INDUSTRY.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection of Pasteurisation of Sour Cream by the Amylase Test. T. Forgács and I. Radics. (*Z. Unters. Lebensm.*, 1938, **76**, 20–24.)—Formerly, sour cream was prepared by the removal of the fatty layer of spontaneously soured milk, but in modern processes pasteurised skimmed milk is inoculated with the lactic acid bacillus, and the resulting curd is mixed with pasteurised cream to bring the fat-content to 16 per cent. (the Hungarian statutory limit), after which the product is homogenised. The sour cream so produced has an acidity of about 40° (Soxhlet–Henkel scale) and a fat-free dry solid content of 7 to 10 per cent. The amylase test investigated by Bengen and Bohm (*Z. Unters. Lebensm.*, 1935, **69**, 146; Abst., ANALYST, 1935, **60**, 325) is applied to the examination of these products. Since the high *p*H of sour cream inhibits the enzymic action, the sample is treated with alkali until its acidity is that of fresh milk (6° to 7° Soxhlet–Henkel, *p*H 6·6), and the test is then applied to the ammonium sulphate serum. The procedure is as follows:—The acidity, *a*, of the sour cream is determined and sufficient $N/4$ sodium hydroxide solution is added to 50 g. to reduce its acidity to 7° (Soxhlet–Henkel). The mixture of 50 g. of sour cream and $\frac{a-7}{2}$ ml. of $N/4$ sodium hydroxide solution is shaken with one-fifth of its weight of solid ammonium sulphate and filtered. The clear filtrate is mixed with Rothenfüsser's starch solution (*Z. Unters. Lebensm.*, 1934, **67**, 396; 1935, **69**, 146) in the proportion of 1 ml. of starch solution for every 10 ml. of original undiluted serum and the mixture is allowed to stand at room temperature for 16 to 18 hours.

Two ml. of 0·025 per cent. iodine solution are added to 2 ml. of the mixture, and the colour produced is stabilised by the addition of 0·5 ml. of 5 per cent. acetic acid. When the sample consists entirely of effectively pasteurised ingredients no hydrolysis of the starch takes place and a blue colour appears after the addition of the iodine solution. When unpasteurised milk or cream is present the starch is hydrolysed by the amylase and the colour produced by iodine is yellowish-brown to red. The inactivation temperature of amylase is 55° C. when the time of heating is 30 minutes. Experiments showed that sour cream prepared from ingredients pasteurised at 80° to 85° C. for 1 minute, or at 63° to 65° C. for 30 minutes, did not respond to this test, which indicates that such pasteurisation is efficient. The method distinguishes between products containing 25 per cent. of unpasteurised ingredients and those prepared from ingredients pasteurised by heating for at least 30 minutes at 55° C. or 5 minutes at 65° C., but does not indicate the exact pasteurisation temperature. A. O. J.

Changes in the Composition of Cheese on Prolonged Keeping. J. Pien and G. Maurice. (*Ann. Falsif.*, 1938, **31**, 136–142 (*cf. Ann. Falsif.*, 1935, **28**, 535).) —Analyses of 50 Camembert cheeses from the same factory were made within 2 days after finishing, and after one, two, three, five and a half, seven and a half, eleven and thirteen months. The following constituents were determined:— moisture, mineral matter, fat, total nitrogen, soluble nitrogen and ammoniacal nitrogen. Moisture diminished from 53 to 15 per cent., but at the same time there was a formation of volatile substances which were lost during drying. During the same period the proportion of fat increased from 22·4 to 43·4 per cent. Calculated on the dry substance the proportion of fat increased gradually from 47·7 to 56·2 per cent. in 11 months, and then decreased to 51·2 per cent. in the next two months, probably owing to incipient saponification. Thus cheese complying with the statutory requirements when analysed may not have done so when first made. Camembert cheese should contain 40 per cent. of fat calculated on the dry substance; if it contained 42 to 43 per cent. of fat when analysed, it may have had less than the statutory 40 per cent. to begin with. The non-fatty solids, expressed as percentages of the total dry solids, diminished from first to last. Lactose and lactic acid decreased from 4·4 per cent. to 0 in less than 2 months. As a result of the fermentation of the lactose the proportion of nitrogenous substances (expressed as casein) increased at first from 41 to 43 per cent. and then, after a few weeks, diminished progressively to 34 per cent. The proportion of soluble nitrogen reached 41·5 per cent. of the total nitrogen, and ammoniacal nitrogen constituted up to 60 per cent. of the soluble nitrogen. Quantitative conclusions as to ammoniacal nitrogen cannot be drawn, since a considerable amount is certainly lost by volatilisation. The only check to the progressive loss of the dry substance of soft cheese samples (which may attain 15 per cent., with a corresponding rise in fat of nearly 9 per cent. on the dry solids) would appear to be to add an antiseptic capable of arresting all microbiological activity. D. G. H.

Oxidation and Reduction in Wines and Beer. J. Ribereau-Gayon. (*Brass. Français*, 1938, **2**, 116–119; *J. Inst. Brewing*, 1938, **44**, 282–283.)—This is a summary of a book by the above-named author, entitled *Oxydations et*

Reductions dans les Vins, the contents of which are said to apply equally to beer. The author has investigated the behaviour of dissolved oxygen in wine under the conditions normally obtaining, the determination of the amount dissolved being made by titration with hydrosulphite in the presence of indigo-carmine. Normally, 6·0 ml. of oxygen per litre are soluble, but this is modified by the presence of carbon dioxide or sulphur dioxide, and by bottling and storage as described. The way in which oxidation by dissolved oxygen is effected is studied. The loss of oxygen in solution in unit time or the oxidising activity is determined by plotting a graph. Sulphur dioxide naturally acts as an anti-oxidant by fixing dissolved oxygen; this combination and the oxidation of the normal constituents is largely influenced by catalysts, particularly ionised copper and iron, copper being the more active of the two. Oxidation is aided by light and heat. The metal catalysts behave as carriers of oxygen for which the oxidisable bodies are the acceptors, direct oxidation not being possible. Ferric iron can be present only when dissolved oxygen is present, and copper can stay in solution only in the cupric state, cuprous salts being insoluble; the natural reducing action of wine gradually eliminates copper. The presence of copper increases the catalytic activity of iron. Wines containing more than 10 to 12 parts of ferric iron per million are liable to form a haze; copper when present to the amount of 0·5 to 0·6 parts per million may give rise to haze upon reduction. Light and heat favour the copper haze and tend to inhibit the iron haze. In conclusion, suggestions are made for the treatment of wines susceptible to iron or copper haze. D. R. W.

Quince Seed Oil. J. Pritzker and R. Jungkunz. (*Z. Unters. Lebensm.*, 1938, **76**, 40–41.)—The two samples of quince seed oil investigated were freshly extracted with ether from commercial samples of quince seed, one being of Swiss origin and the other probably of Russian or Spanish origin. The Swiss seed contained 90 per cent. of pear quince seed and 10 per cent. of apple quince seed. In the results given below the first figure refers to the Swiss seed oil and the second to the seed oil of Russian or Spanish origin. Sp.gr., 0·9262, 0·9118; Zeiss butyroref. no., at 40° C., 60·3, 52·3; acidity, 38·1, 223·7; acid value, 21·4, 125·5; ester value, 164·9, 159·7; saponification value, 186·3, 185·2; iodine value (Hanus), 113·4, 114·5; Reichert–Meissl value, —, 0·5; Polenske value, —, 0·3; unsaponifiable matter (Spitz and Hönig), 1·64, 0·96 per cent.; unsaponifiable matter (Bertram), 1·54, 0·86 per cent.; phytosterol (minimum), 0·66, 0·39 per cent.; m.p. (uncorr.) of the phytosteryl acetate, 118° C., 116° C. The total fatty acid content was 95·5, 95·4 per cent. The fatty acids liquid at ordinary temperature had:—Zeiss butyroref. no., at 40° C., 48·5, 49·0; neutralisation value, 195·0, 194·1; mean molecular equiv. 287·7, 289·0; solid fatty acids in the original oil (Grossfeld), 16·4, 17·8 per cent.; solid fatty acids in the original oil (Bertram), 9·4, 8·9 per cent. With each sample the Bellier test gave a negative and the Kreis test a faintly positive result. The oil from Swiss seed was of a greenish colour and the other was greenish-brown. Both oils resembled rape oil in taste and odour. The differences in the figures for refraction and sp.gr. are apparently due to the high acid value of the second oil. Quince seed oil is very similar to apple seed and pear seed oils but, whilst these contain only a trace of iso-oleic acid, quince seed oil was found by Grossfeld's method to contain about 11 per cent.

This is confirmed by the difference in the figures for the solid fatty acids found by the methods of Grossfeld and of Bertram. The low Reichert–Meissl value raises doubt concerning the statement of Grün and Halden (*Analyse der Fette und Wachse, II*, 236), that quince seed oil contains myristic acid. A. O. J.

Composition of the Wax-like Substance Extracted from the Coffee Berry. H. Wagner. (*Z. Unters. Lebensm.*, 1938, **76**, 1–20.)—The wax-like substance in the outer layers of the epidermis of the seed-coat of the coffee berry, which is a by-product in the preparation of caffeine-free coffee, contains fatty and resinous bodies. Owing to the difficulty and expense of its purification on the large scale as well as its unpleasant odour it is, at present, of little commercial value. It is a dark brown brittle substance, covered with a white incrustation of caffeine. Two specimens differed in colour (grey-green and brown), in moisture-content (6 per cent. and practically none), in m.p. (68° C. and 55° C.) and in ash (0·22 and 0·50 per cent.), but gave the same amount of dry substance soluble in petroleum spirit (48·78 and 48·34 per cent.), and the residues after extraction had the same indefinite m.p. (74° to 79° C.). The wax dissolves readily in alcohol, benzene, chloroform, acetone and glacial acetic acid but is less soluble in ether. It cannot be recrystallised from these solvents. It contains protein, phytosterol and phosphorus and sulphur compounds. When evaporated with conc. hydrochloric acid and industrial alcohol (but not pure alcohol) it forms a deep but not permanent Bordeaux-red colour, which is extracted by chloroform or benzene but not by ether. This reaction is given by the petroleum spirit extract but not by the residue. With a mixture of hydrochloric and glacial acetic acids it gives a deep green colour. Its iodine value is 93·15 and it is readily saponified with alcoholic alkali but only with difficulty with aqueous alkali. Successive extraction with solvents gave the following figures per cent.:—cold petroleum spirit, 48·8; cold ether, 22·4; warm ether, 12·4. The remaining 16·4 per cent. was a resinous body partly soluble in benzene, leaving a dark lacquer-like substance which, with the exception of some vegetable debris, was soluble in chloroform. Distillation of the wax with steam gave an oily product. A. O. J.

Reactions of *Helvella Esculenta*. G. Reif. (*Z. Unters. Lebensm.*, 1938, **76**, 30–36.)—It has been shown previously (*Z. Unters. Lebensm.*, 1935, **69**, 585; Abst., ANALYST, 1935, **60**, 707) that the fungus *Helvella esculenta*, unlike the edible morels (*Morchella esculenta, M. conica* and *M. semilibera*), contains a substance with a high reducing power sufficient to liberate selenium from a solution of selenious acid in sulphuric acid and to react with a reagent containing phosphotungstic and phosphomolybdic acids and with fuchsin decolorised by sulphurous acid. When the fungus is dried at temperatures up to 120° C., or when it is stored in evacuated vessels even for two or three years, its reducing power is not diminished. Experiments showed that the absence of reducing power in the commercial product is due to the method of storage, the essential conditions for the uncooked fungus being free access of air or oxygen and the presence of a minimum amount of water. The reducing power was measured by mixing 1 g. of the dried powdered fungus with 40 ml. of water, 10 ml. of 10 per cent. sodium hydroxide solution and 5 g. of

sodium chloride and distilling 30 ml. Ten ml. of the distillate were acidified with 5 ml. of glacial acetic acid and titrated with 0·1 per cent. potassium permanganate solution. Under these conditions the distillate from the fresh fungus requires about 1·2 ml., and that from the fungus stored under conditions promoting loss of reducing power about 0·12 ml. of permanganate solution. When the fungus was stored in dry air, dry oxygen, dry nitrogen or moist nitrogen no diminution of reducing power occurred, but in humid air or oxygen the reducing power decreased at first rapidly and then more slowly. Separate experiments upon portions of the plant showed that the stalks retained their reducing power longer than the caps. Samples bought in the market gave low figures for the reducing power which, since it had attained its minimum value during storage in moist air, was not further affected by the conditions which promote diminution in the fresh fungus. As a rule, the fungus on the market is the previous year's crop. In preparing the canned product, the fungus is boiled in water, the water being poured away and fresh water added. This procedure removes the reducing substance. A product known as *Leipziger Allerlei* (Leipzig All-sorts) contains vegetables such as peas, carrots and asparagus as well as Helvella, and since the fungus is a spring crop and the vegetables are autumn crops, the fungus will have been dried and stored for at least several months. The examination of the reducing action of such a product must be made upon the distillate, to eliminate the effect of tannins present in the vegetables. The dried and stored commercial fungus and the fungus which has been boiled with water are not poisonous, and the loss of toxicity corresponds with loss of reducing power. The toxic substance is not similar to that of *Amanita* spp., which gives a dark greenish-blue colour with *m*-nitrobenzaldehyde. Helvella extracts give a grey-brown colour, which is also given by the non-toxic morel. It is suggested that the toxic substance in Helvella is aldehydic and alkaloidal in character. A. O. J.

Semi-Micro Method for the Conductometric Determination of Nicotine. R. R. Tilici and F. Cristea. (*Z. Unters. Lebensm.*, 1938, **76**, 44–51.)—The standard gravimetric method for the determination of nicotine by precipitation with silicotungstic acid can be adapted to conductometric measurement if the presence of excess of mineral acid is avoided. The method described below has the advantage that it occupies little time, since it is not necessary to wait 24 hours for the precipitate to crystallise. It is applicable to the direct determination of all bases and alkaloids which form insoluble compounds with silicotungstic acid. In the experiments nicotine bitartrate was used in concentrations of the order obtained by the distillation of 2 g. of tobacco. The procedure for the determination of nicotine in alkaline solution is as follows:—The solution is slightly acidified to methyl red with either acetic or tartaric acid and 0·4 ml. of 0·1 *M* hydrochloric acid is added for every 8 mg. of nicotine present. The determination is carried out conductometrically in the usual way with 0·25 *M* silicotungstic acid solution by means of a micro-burette graduated in 1/100 ml. When tartaric acid is used the graph shows two intersecting straight lines, the point of intersection being the equivalent point corresponding with the formation of $2C_{10}H_{14}N_2.H_8[Si(W_2O_7)_6].3H_2O$. When acetic acid is used the line has two turning points, the first corresponding

with the formation of $4C_{10}H_{14}N_2.H_8[Si(W_2O_7)_6].xH_2O$ and varying with the concentration of acid, and the second corresponding with the formation of $2C_{10}H_{14}N_2.H_8[Si(W_2O_7)_6].3H_2O$, and this point always coincides with the point of equivalence. Although acetic acid is the weaker acid, the use of tartaric acid has the advantage of avoiding the formation of the basic salt. If the nicotine is in acid solution it is made distinctly alkaline to thymol blue by the addition of 0·01 *M* sodium hydroxide solution, and a slight excess of tartaric acid is added (0·1 ml. of *N* tartaric acid solution for each 6 mg. of nicotine) and 0·4 ml. of 0·1 *M* hydrochloric acid for each 8 mg. of nicotine. The procedure is then as previously described. This method gives results agreeing well with parallel determinations made by the gravimetric method. A. O. J.

Colorimetric Estimation of Nicotinic Acid Amide. P. Karrer and H. Keller. (*Helv. Chim. Acta*, 1938, **21**, 463–469.)—When pyridine compounds are treated with 2: 4-dinitro-1-chlorobenzene and the reaction mixture is made alkaline, an orange-red solution is produced. This well-known colour reaction is the basis of a quantitative method of estimating nicotinic acid amide (together with nicotinic acid) in biological material of animal origin, from which other derivatives of pyridine are absent. The method is not, however, applicable to vegetable extracts which may contain other pyridine derivatives. The final colour was measured in a "Leifostufenphotometer" and in a Rosenheim–Schuster tintometer, calibration curves with pure nicotinic acid amide being constructed for each instrument. Different amounts of the amide, from 1 to 25 mg., were heated with four times the amount of 2: 4-dinitro-1-chlorobenzene for 1 hour at 90° C. The product of the reaction was extracted with ether to remove unchanged dinitrochlorobenzene, and the ether-insoluble matter was dissolved in water. The ethereal extracts were washed two or three times with water, and the combined aqueous solutions were warmed to remove dissolved ether, and filtered to remove any traces of dinitrochlorobenzene precipitated after removal of the ether. The solution was then made up to a definite volume, and the required amount was transferred to the colorimeter tube. One or two drops of 20 per cent. potassium hydroxide solution were added and the colour was measured. Accurate results were obtained with mixtures of the amide with ten times its weight of sugar or gelatin. The estimation was made by extracting the dry mixture with hot benzene, removing the benzene by distillation, and causing the benzene extract to react with dinitrochlorobenzene as described above. A fairly pure co-zymase preparation was also assayed in the same way; its nicotinic acid amide content was found to be 7·5 per cent. Ox-liver was extracted with hot water, and the aqueous extract was evaporated to dryness and heated for an hour with 0·1 *N* potassium hydroxide solution; this was neutralised and evaporated to dryness. The residue was extracted with hot benzene and the extract was treated as described above. The nicotinic acid amide content of fresh liver was found to be 4·5 mg. per kg. F. A. R.

New Method of Identifying Barbituric Derivatives. M. Pesez. (*J. Pharm. Chim.*, 1938, **28**, 69–82.)—The following procedures are recommended :—*Identification of solid barbiturates.*—A few mg. of the barbituric derivative are introduced into a dry centrifuge tube with 2 to 3 ml. of pure methyl alcohol and shaken

gently until dissolved. Two drops of a cobalt and calcium reagent (containing 1 g. of cobalt nitrate, 1 g. of calcium chloride and 10 ml. of water) are added, and, after mixing, 1 drop of 5 per cent. sodium hydroxide solution. On agitation there forms a blue colour and then an indigo-blue precipitate. After centrifuging or sedimentation the liquid is decanted and the residue is treated with 2 to 3 drops of dilute hydrochloric acid. Then, after very gentle agitation, the liquid is poured on to a microscope slide and examined, after 1 or 2 minutes, with a magnification of × 50 to 60. If necessary, the barbiturate can be recrystallised by dissolving it on the slide in 1 drop of ammonia solution, followed by 2 or 3 drops of dilute (1 : 5) hydrochloric acid and mixing.

Identification in solid therapeutic preparations.—About 20 mg. of the preparation are treated in a centrifuge tube with 2 or 3 ml. of methyl alcohol. The contents of the tube are mixed with a very thin stirrer, heated to boiling and centrifuged. The liquid is decanted into another centrifuge tube and examined as described above. Sodium salts and compounds with pyramidone and diethylamine can be treated in this way. Calcium salts (such as Phanodorm-calcium) are boiled with 2 or 3 drops of methyl alcohol and 1 drop of 50 per cent. acetic acid and then centrifuged. Two drops of 50 per cent. sodium hydroxide solution are added to the supernatant liquid.

Identification in solution.—With concentrated solutions (injectable narcotic solutions of Veronal or Numal) 2 or 3 drops of the solution are added to 3 ml. of methyl alcohol and then treated with the reagent. With dilute solutions the barbiturate is preferably isolated by acidifying with dilute sulphuric acid and then agitating with ether; evaporation of the ether yields a residue to which the test reaction may be applied.

Detection in urine.—To 100 to 200 ml. of the urine are added 5 ml. of aqueous tartaric acid solution (1: 5) and then 40 ml. of ether. The liquid is shaken vigorously and, after standing for a few minutes, the ethereal layer is separated. Two further extractions, each with 20 ml. of ether, are made. The ethereal solutions are united, left in contact with anhydrous sodium sulphate for a few moments, decanted and evaporated, giving a residue which is then dissolved in 2 to 5 ml. of methyl alcohol. Three ml. of this solution are used for the reaction.

Detection in blood.—The method of Chéramy and Lobo (*J. Pharm. Chim.*, 1934, 461) is recommended. The clot from 50 ml. of blood is ground with sand and treated with acetone. The mixture is transferred to a large conical flask, and the serum and acetone are added (making 20 ml. in all). After acidification with 20 per cent. tartaric acid solution the liquid is boiled on a water-bath for 30 minutes, cooled, filtered and distilled on a water-bath. Fifteen per cent. ammonium sulphate solution is added to the residual liquid, which is then filtered and extracted with ether. The ethereal solution is separated from the aqueous layer, dried over anhydrous sodium sulphate, and evaporated in a weighed vessel, the reaction being then applied to the residue of barbiturate.

Detection in viscera.—The method of Fabre and Fredet (*J. Pharm. Chim.*, 1925, 2, 321) is the best. The pulped organ is diluted with 5 times its weight of water, and the mixture is boiled for a few seconds to destroy the antitrypsin. After cooling to 50° to 55° C., the mixture is treated with pancreatin in the propor-

tion of 1 g. of the enzyme to 50 g. of pulp, and kept at 50° to 55° C. for 10 to 12 hours, after which it is boiled and filtered, and the filtrate is extracted with ether in an acid medium. The ethereal extract is evaporated and the residue is weighed, dissolved in methyl alcohol and submitted to the reaction.

The typical crystalline formations obtained with diethylmalonylurea (Veronal), ethylbutylmalonylurea (Soneryl), diallylmalonylurea (Dial), allyl*iso*butylmalonylurea (Sandoptal), allyl*iso*propylmalonylurea (Numal), cyclopentenylallylmalonylurea, phenylethylmalonylurea (Gardenal, Luminal), phenylmethylmalonylurea (Rutonal), and cyclohexenylethylmalonylurea (Phanodorm) are described, with diagrams. After identification of the barbituric derivative by the crystalline formation, confirmation may be obtained by specific reactions. E. M. P.

Biochemical

Introduction to the Biochemical Study of Pneumonoconiosis. R. Fabre and E. Kahane. (*Archives des Maladies Professionelles*, 1938, **1**, 21–28.)—In order to obtain information of value in the study of silicosis the mineral contents of the lungs of 33 healthy individuals who had died as the result of accident were investigated qualitatively and quantitatively. No mineral particles were found in the lungs of a foetus and a month-old baby and only a small amount in the lungs of two children. Of 28 adults, the lungs of 9 contained under 10 mg. of siliceous particles per 100 g. of tissue, and the rest contained from 10·2 to 43·6 mg., with an average of about 20 mg. per 100 g. The amount of silica in the siliceous particles was remarkably constant, being from 81 to 93 per cent. in the adults. It would seem therefore that of all the different kinds of particles inhaled, particles of quartz are most tenaciously retained by the lungs. Experiments carried out with rabbits to which siliceous dusts of various types were administered intratracheally have shown that the amount of dust in the lungs does not decrease within the first few weeks after administration, but shows an appreciable decrease after 3 months; it is not yet known how the dust is eliminated. In further experiments rabbits, guineapigs and rats were given prolonged exposures to a sandstone dust, and the lungs finally contained up to 1·2 per cent. The presence of silica was also established in the liver, the suprarenals, the kidneys, the heart, the brain and the blood; it is fairly certain that this originated in the dust inhaled by the animal and transported from the lungs in the bloodstream. Researches have also been made on the amount of carbonaceous particles in the lungs of normal human beings. The amount of carbon found in the lungs of 10 adults varied from 17 to 146 mg. per 100 g. of tissue with an average value of 66 mg. per 100 g. Animal experiments have shown that where prolonged exposure to carbon dust has taken place, carbon is also found in the liver and the kidney, and occasionally in the spleen and testicles. When manganese dioxide is inhaled, this readily passes into circulation, in contrast with the behaviour of silica and carbon; it may then produce the condition known as "manganism." F. A. R.

Determination of Bromide in Tissues and Biological Fluids. B. B. Brodie and M. M. Friedman. (*J. Biol. Chem.*, 1938, **124**, 511–518.)—The following method is recommended for the determination of quantities of the order

of 0·060 to 2·0 mg. of bromide, the average error being less than 1 per cent. Two hundred mg., or less, of dried tissue are weighed into a 30-ml. nickel crucible (1¾ inches in height) and covered with 3 g. of sodium hydroxide pellets. This crucible is placed in a 100-ml. nickel crucible, the bottom of which is covered with a layer of sand about 0·5 cm. thick, and the larger crucible is supported by metal cross-bars in an iron cylinder similar to that described by Kendall in his iodine method (*J. Biol. Chem.*, 1914, **19**, 251; 1920, **43**, 149) and placed over a No. 3 Meker burner. The outer crucible is heated at a low temperature, which is gradually raised to red heat, the fusion being carried out without excessive foaming. When the contents have settled to the bottom of the crucible and very few bubbles are being liberated, potassium nitrate is added, a few mg. at a time, until all organic matter is destroyed, as shown by the absence of bubbling on the further addition of potassium nitrate. The crucible is carefully rotated so as to wash down any organic matter which may have climbed up the sides, and replaced over the burner. A crystal of potassium nitrate is added and if no bubbling occurs the fusion is complete. A few carbon particles which may remain after the addition of the nitrate do not affect the accuracy of the results. The crucible is rotated to allow the melt to solidify on the sides and cooled, the contents are treated with 15 ml. of warm water, and the crucible is placed in an oven at 100° C. for 30 minutes. The solution is transferred first to a beaker and then to a conical flask, the volume is adjusted to about 30 ml., the liquid is cooled, and 2·0 ml. of conc. sulphuric acid (sp.gr. 1·84) are cautiously added drop by drop down the side of the flask. After cooling, a further 0·3 ml. of conc. sulphuric acid is added, and then sodium carbonate, in small quantities, until it is present in excess. The liquid is treated with 2 g. of sodium dihydrogen phosphate and 6 ml. of *N* sodium hypochlorite solution (1 ml. for every 5 ml. of solution), the flask is immersed in a boiling water-bath for 10 minutes, and the excess of hypochlorite is then destroyed by adding 5 ml. of 50 per cent. sodium formate solution, washing down the sides of the flask with water, and replacing on the water-bath for 5 minutes. After cooling, the liquid is transferred to a 500-ml. wide-mouthed conical flask, diluted to 160 ml., treated with 10 g. of sodium dihydrogen phosphate and 40 ml. of 6 *N* sulphuric acid and cooled to 10° C. Three drops of 10 per cent. ammonium molybdate solution and 1 g. of potassium iodide are added and the liquid is shaken. As soon as the potassium iodide dissolves the liberated iodine is titrated with 0·005 *N* sodium thiosulphate solution, starch indicator being added near the end-point. A blank determination is made under identical conditions, water being substituted for the bromide solution. The sodium thiosulphate solution should be standardised under the conditions of the determination. For this standardisation a 0·01 *N* bromate solution is accurately measured into a 500-ml. conical flask and to it are added 5 ml. of 50 per cent. formate solution, 12 g. of sodium dihydrogen phosphate and 40 ml. of 6 *N* sulphuric acid. The volume is adjusted to 200 ml. with water, the liquid is cooled to 10° C., 1 g. of potassium iodide and 3 drops of 10 per cent. molybdate solution are added, and the liberated iodine is titrated with the sodium thiosulphate solution. The end-point can easily be seen if the flask is placed in a box which is illuminated from an upper back corner with a 60-watt lamp; the inside of the box is painted white and the flask is held obliquely against the side

of the box opposite to the lamp. The use of an indicator in neutralising the alkali results in a loss of bromine, possibly because of bromination of the indicator oxidation products; a moderate excess of sodium carbonate does not affect the oxidation of bromide, since the solution is subsequently buffered by a large amount of sodium dihydrogen phosphate.

In analysing biological fluids, a quantity of up to 1 ml. of blood or 3 ml. of serum, urine or saliva is pipetted into the crucible, a pellet of sodium hydroxide is added, and the material is dried in an oven at 100° C. The procedure is then the same as with dried tissues. In test experiments with quantities of bromide ranging from about 0·07 mg. to 1·9 mg., the average amounts recovered ranged from 98·9 to 100·3 per cent. The method can be used for the determination of similar quantities of iodide. E. M. P.

Iodine Survey of New Zealand Live-Stock. Part III. Sheep of the Canterbury District. E. Mason and D. F. Waters. Part IV. Sheep of the Marlborough, Nelson and Westland Districts and Review of the South Island. D. F. Waters. (*Trans. Roy. Soc. New Zealand*, 1936, **66**, 143–177; 1937, **67**, 463–474.)—The iodine-contents of groups of lamb thyroids from known localities all over South Island, New Zealand, were determined by the method of Leitch and Henderson (*Biochem. J.*, 1926, **20**, 1003), and the results were expressed as per cent. of dry weight. The average moisture-content of lamb-thyroids was 75 per cent. The following details were obtained for each sample and an attempt was made to correlate the information with the iodine-contents of the thyroids: locality of farm, type of country, type of soil, licks supplied, manurial treatment and supplementary feeding. In Canterbury province the iodine-contents of the thyroids tended to be slightly higher in animals from districts where the rock was basic igneous than from districts where the rock was miocene, trias-jura and alluvium; the average figures were 0·28, 0·22, 0·20 and 0·18 per cent. (on the dry weight) respectively. Otherwise there was no correlation between the iodine-content and soil type. The variations between the different districts of South Island were very wide, and there were large differences in adjacent districts of the same province. The Otago results showed particularly wide variations, and 8 per cent. of the glands examined were deficient in iodine, *i.e.* contained below 0·10 per cent.; on the other hand, 20 per cent. of the samples contained over 0·4 per cent. of iodine—a greater proportion of high samples than was found in any other district. Less variation was found in the results from Nelson and Marlborough, which were very similar to one another; 50 per cent. of the samples contained more than 0·23 per cent. of iodine. Banks Peninsula (in Canterbury), also gave satisfactory values. Canterbury (with the exception of Banks Peninsula and the limestone area of Wairarapa) showed no high values, but only 10 per cent. of the samples were below the critical value of 0·10 per cent. Thyroids from Westland, Southland, Buller Valley (in Nelson) and the Grey Valley (in Westland) gave progressively lower iodine values in that order, and these three districts are regarded as liable to outbreaks of goitre. The area most deficient in iodine was Totara Flat in the Grey Valley, where 50 per cent. of the samples were found to contain less than 0·05 per cent. of iodine.

F. A. R.

Fixation of Arsenic Compounds *in vitro* by the Red Corpuscles of the Blood. M. J. Thubet. (*J. Pharm. Chem.*, 1938, **28**, 22–30.)—The distribution of arsenic compounds between the plasma and the corpuscles of horse's blood was measured by determining the arsenic-content of the whole blood and of the supernatant liquid after centrifuging. It was found that three compounds containing quinquevalent arsenic, *viz.* sodium arsenate, sodium cacodylate and atoxyl, were not absorbed from plasma by blood corpuscles. On the other hand, three compounds containing tervalent arsenic, *viz.* sodium arsenite, phenylarsine oxide and neosalvarsan were taken up by the red corpuscles. The first two substances were strongly absorbed, especially the second; they were found to be present in much greater concentration in the corpuscles than in the plasma. The reverse was found with neosalvarsan. The amount absorbed by the corpuscles varied with the concentration of arsenic and the distribution followed Freundlich's law exactly. The phenomenon was thus one of adsorption, and was reversible, for on shaking corpuscles containing adsorbed arsenic with fresh plasma a redistribution of the arsenic took place. Adsorption was immediate, and the amount adsorbed did not vary with the time of contact. F. A. R.

Inhibition of the Carr and Price Reaction for Vitamin A by Substances in Cod-liver Oil. A. Emmerie. (*Rec. Trav. Chim. Pays-Bas*, 1938, **57**, 776–780.) —The substance inhibiting the Carr and Price reaction was prepared as described in an earlier paper (*Nature*, 1933, **131**, 364), except that the extraction with sulphuric acid and regeneration with water and petroleum spirit were repeated 3 times; 43 g. of reddish-brown material were thus obtained from 10 litres of cod-liver oil. This oily material was esterified with absolute methanol and dry hydrochloric acid gas at 0° C. Seven fractions were obtained by distillation *in vacuo*, and each of these had about the same inhibiting power, which was measured by adding definite quantities of the appropriate esters or acids to a solution of the unsaponifiable fraction of halibut-liver oil in chloroform, diluted so that 0·15 ml. mixed with 1·5 ml. of antimony chloride solution gave a Lovibond tintometer reading of 6 blue units. The Lovibond reading was reduced by addition of 1·2γ of ester per 0·15 ml. to a reading of 5·4; by 2·4γ to 4·5; by 6γ to 4; by 30γ to 3; by 120γ to 2. The hydrogenated esters had no inhibiting power. The fractions were pale yellow viscous liquids which did not solidify at —30° C. The equivalent weights of three fractions were respectively 328, 335 and 348; all were unsaturated and the bromine values of two were determined. On oxidation of the saponified esters of fractions 5 and 7 with aqueous potassium permanganate solution, decane-1 : 10-dicarboxylic acid was isolated. The ultra-violet absorption of the fractions was also examined. D. G. H.

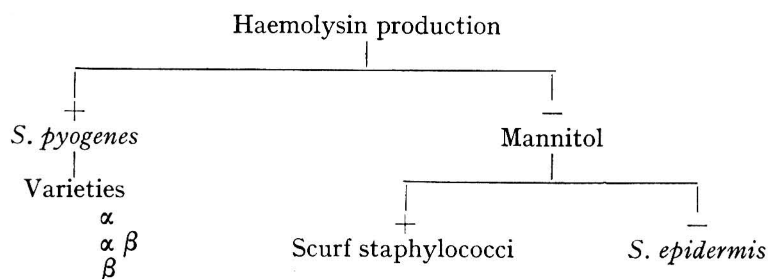
Detection of *d*- and *l*-Phenylalanine in Biological Fluids. K. Closs and S. D. Henriksen. (*Z. physiol. Chem.*, 1938, **254**, 107–114.)—A suspension of *B. proteus* converts *l*- but not *d*-phenylalanine into phenyl-pyruvic acid, and an extract prepared from rat-kidneys converts *d*- but not *l*-phenylalanine into phenyl-pyruvic acid. These reactions are used to determine the presence of the one or the other isomer in a solution, any phenyl-pyruvic acid or phenyl-lactic acid that may be present being first removed by continuous extraction with ether. In testing for the presence of *l*-phenylalanine, the solution (1 ml.) is freed from

ether, a drop of 0·1 per cent. phenol red solution is added, and then sufficient 0·1 *M* sodium carbonate solution to make the solution bluish-red (*p*H 8–9). A suspension of washed *B. proteus* (5 ml. containing about 100,000 million organisms per ml.) in 0·5 per cent. potassium acetate solution is added, and the tube left for half an hour at room temperature in a sloping position to allow of the maximum surface area being exposed to the air. Sufficient 10 per cent. sulphuric acid is then added to turn the solution first yellow and then red, after which it is saturated with ammonium sulphate; this precipitates protein, adjusts the *p*H and increases the intensity of the colour produced on subsequent addition of the iron salt. Finally, 7 to 10 drops of half-saturated iron ammonium alum solution are added. The formation of a green colour indicates the presence of *l*-phenylalanine in the original solution. The detection of *d*-phenylalanine is carried out by exactly the same method, except that an extract prepared in the following way is used in place of the bacterial suspension:—Fresh rat kidneys are minced and washed with 0·5 per cent. potassium acetate solution. The tissue is then triturated with more of the potassium acetate solution in a mortar and the suspension is centrifuged. The deposit is extracted once more, and the combined aqueous solutions form the enzyme preparation used in the test. F. A. R.

Erratum.—SPECTROGRAPHIC STUDIES ON THE ANTIMONY TRICHLORIDE REACTION FOR VITAMIN A.—On page 612 (August issue), line 27, *for* "693$m\mu$ band" *read* "603$m\mu$ band."

Bacteriological

Classification of the Staphylococci by Precipitation and Biological Reactions. S. T. Cowan. (*J. Path. and Bact.*, 1938, **46**, 31–45.)—The majority of strains examined were of human origin, but strains of animal origin and miscellaneous strains isolated from food were included. The tests employed were: pigment production, fermentation of mannitol, liquefaction of gelatin, the Voges–Proskauer reaction, haemolysin production, coagulase production, and serological tests by means of the precipitin reaction (*i.e.* the precipitation by the blood serum of immunised rabbits resulting from admixture with an extract of the growth of an organism of the same type as that with which they were immunised). Complete correlation between the production of α- or β-haemolysin and coagulase was shown. It was found that certain of the above-mentioned tests based on metabolic activities could be eliminated, and the method of classification suggested, based on that of Andrewes and Gordon but modified chiefly by the inclusion of haemolysin production, is indicated by the following schema:



In the serological investigation rabbits were immunised against a strain of *Staph. pyogenes* α isolated from apleural effusion and others against a strain of *Staph. epidermis* isolated from healthy skin. These were called group A and group B respectively. Antigens were prepared from 157 strains and put up against group A and group B sera, and, if no reaction was obtained, against group C and Group D sera prepared from other strains. (The group C serum was prepared from *S. pyogenes* which reacted only slightly with group A serum.) The following table shows the correlation of the biological and serological classification of staphylococci:

	Serological group				
	A	B	C	D	X
S. pyogenes α	84	0	14	0	0
" αβ	11	0	1	0	0
" β	0	3	0	0	1
Scurf staphylococci	0	3	0	2	7
S. epidermidis	0	17	0	1	13

The three strains of group D were derived from infected urine, vulvitis and the cervix.

From this it is evident that the majority of strains of *S. pyogenes* α and *S. pyogenes* αβ fell into one serological group, *viz.* A. There were, however, 15 strains which could not be classified by the sera available; these have tentatively been grouped together and may possibly prove to be heterogeneous on further study. The non-haemolysin-producing strains appear to be the more heterogeneous serologically; while 20 fell into one group and 3 into another, the remaining 20 were not classified. D. R. W.

Agricultural

Ignition at Low Temperatures of the Organic Matter in Soils. J. S. Hosking. (*J. Agric. Sci.*, 1938, **28**, 393–400.)—The low temperature ignition of soil organic matter has been investigated for temperatures ranging from 100° to 500° C. The soils used were 4 Australian and 1 English, together with a sample of Merck's "humic acid" and one of cellulose (filter-paper). Loss of organic matter at 100° C. may be quite appreciable, so that so-called "moisture" figures include a proportion of organic matter. Thus, more than a third of the 7 per cent. loss at 100° C. of the "humic acid" was due to organic carbon. Below 200° C. losses are mainly due to distillation of volatile constituents of the organic matter. Between 200° and 300° C. the main reaction is destructive distillation with carbonisation of the residue, and above 300° C. the reaction is chiefly ignition of this carbonaceous material. Cellulose showed only small losses below 200° C., but a temperature of 400° C. for 16 hours was necessary for complete ignition. The "humic acid" contained 40 per cent. of constituents volatile below 200° C.; complete ignition occurred at 360° C. Approximately 85 per cent. of the organic matter of soils and humus is removed at temperatures up to 300° C., and at this point the effect of the inorganic material in the soils and their texture becomes appreciable in reducing the rate of removal of the remaining organic matter. Two hours' heating at 450° C., or half an hour at 500° C., are recommended for the removal of 99 per cent. of soil organic matter. D. G. H.

Chemical Evaluation of Pyrethrum Flowers (*Chrysanthemum cinerariaefolium*). A Comparison of Several Methods. J. T. Martin. (*J. Agric. Sci.*, 1938, **28**, 456–471.)—Comparative analyses of pyrethrum flowers have been made by five methods; Tattersfield *et al.* (*J. Agric. Sci.*, 1929, **19**, 266; Abst., ANALYST, 1929, **54**, 351); Seil (*Soap*, 1934, **10**, 89); Ripert (*Ann. Falsif.*, 1934, **27**, 312); Haller and Acree (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 343) and Wilcoxon (*Contrib. Boyce Thompson Inst.*, 1936, **8**, 175). The methods were examined and compared in detail and agreed in giving the relative proportions of pyrethrins in the samples, but not in the absolute values of the pyrethrins 1 and 2. In fact, the discrepancies were such that until standard methods of determination are agreed upon the method used should be stated. Higher figures were obtained by the Wilcoxon method for pyrethrin 1 than by the Seil method, and the greatest discrepancies occurred with the richest flowers. Further work is required in the Wilcoxon process to account for the non-linearity of the relationship between the iodate required and the monocarboxylic acid present as the latter increases in amount. The figure for pyrethrin 2 determined by the Haller and Acree method appears to vary with the origin of and method of drying the flowers, and in some instances was below and in some above those given by the Seil method. Ripert's method gave rather higher figures than Seil's for pyrethrin 1, but both methods appear to have the same sources of inherent error. It is probable that there is some loss of pyrethrin 1 by the Tattersfield method owing to the action of the sulphuric acid during distillation. Some work on the effect of the solvent used in the initial extraction upon the separation of the pyrethrins has been done. Petroleum spirit extraction for a minimum of 20 hours suffices for the separation of nearly the whole of pyrethrin 1, but whether toxic material is left behind either as adsorbed unaltered pyrethrins or as altered pyrethrins still possessing insecticidal properties can be shown only by toxicity trials. D. G. H.

Organic

Detection of *Iso*propanol in Alcohols. M. Metra, L. Lesage and F. Descatoire. (*Ann. Falsificat.*, 1938, **31**, 218–221.)—The method is based on the oxidation of *iso*propyl alcohol to acetone and the detection of the acetone by a modification of Imbert's colour reaction. To the alcohol to be tested there is added a sufficient quantity of bromine water to effect oxidation according to the equation $CH_3.CHOH.CH_3 + O = CH_3.CO.CH_3 + H_2O$. The tube is placed in the steam from a boiling water-bath in such a manner that the liquid is in the steam and the acetone vapour condenses on the upper part of the tube. When decolorisation is complete, the tube is shaken and cooled, and the contents are treated successively with 1 ml. of glacial acetic acid, 2 ml. of 10 per cent. aqueous sodium nitroprusside solution (freshly made) and 5 ml. of conc. ammonia. If the alcohol contains *iso*propyl alcohol, a violet-red colour develops in the liquid. The colour is easily discernible with 0·05 per cent. of *iso*propyl alcohol. When the *iso*propyl alcohol-content is less than 1 per cent., 5 ml. of the original alcohol are oxidised with 5 ml. of saturated bromine water. When only traces of *iso*propyl alcohol are present, 50 ml. of the alcohol and 50 ml. of bromine water are introduced into a

200-ml. conical flask provided with a Vigreux column cooled by water. The liquid is heated gently until it is completely decolorised and then treated successively with 10 ml. of 30 per cent. sodium hydroxide solution and 10 ml. of 12 volume hydrogen peroxide, followed by refluxing for 5 minutes to destroy aldehydes formed during the oxidation. The liquid is then distilled, and the test reaction is applied to the first 5 ml. of distillate. If the alcohol contains no *iso*propanol a light yellow colour results, whilst in the presence of 0·01 per cent. of *iso*propanol the specific violet-red colour develops.

It is recommended that in the presence of impurities which would vitiate the reaction 200 ml. of the sample, 200 ml. of water and 500 ml. of a saturated salt solution should be well mixed and extracted with carbon tetrachloride (100 ml. in 3 extractions). The liquid is decanted and filtered through a pleated filter-paper, and acetone and other ketones are removed by the method of Hoff and Macoun (ANALYST, 1933, **58**, 749). E. M. P.

Determination of Formaldehyde in Formaldehyde Tanned Leather. J. H. Highberger and C. E. Retzsch. (*J. Amer. Leather Chem. Assoc.*, 1938, **33**, 341–352.)—The method finally adopted for the determination of formaldehyde in formaldehyde-tanned leather was an adaptation of that of Clausen (*J. Biol. Chem.*, 1922, **52**, 263). One to 2 g. of the sample of leather, reduced to a suitably fine state of division, are weighed into a 500-ml. Kjeldahl flask. The lower end of the vertical condenser dips below the surface of the sodium bisulphite solution (12 g. per litre) in a 300-ml. Erlenmeyer flask. The sodium bisulphite solution (freshly made at frequent intervals) required for amounts of formaldehyde up to 0·04 g. is 10 ml.; up to 0·08 g., 25 ml.; up to 0·17 g., 50 ml. Should the amount of formaldehyde determined equal the maximum for the bisulphite used, the determination should be repeated with half the weight of sample or twice the amount of bisulphite solution. One hundred ml. of approximately 2 N sulphuric acid are put into the Kjeldahl flask, and the liquid is distilled until about 10 ml. remain in the flask (45 to 60 minutes). The condenser is washed down, and the receiving flask is stoppered and left for 15 minutes. Starch indicator is added, and 0·1 N iodine solution is run in until the first blue end-point is reached. Ten to 15 ml. of 95 per cent. ethyl alcohol are then added, the flask is well shaken, a quantity of 5 per cent. sodium carbonate solution equal in volume to that of the 1·2 per cent. bisulphite solution taken is added from a graduated cylinder, and the final titration with 0·1 N iodine solution is started as soon as the colour of the first end-point is discharged. If the alkalinity has been correctly adjusted the iodine will be consumed as rapidly as it can be added during the greater part of the titration. When the reaction becomes slower 2 or 3 ml. more sodium carbonate solution is added, and if the iodine consumption is still slow, the end-point is reached by adding the iodine drop by drop. The end-point is quite distinct and phenolphthalein paper should show a definite red colour. Each ml. of 0·1 N iodine solution used in the second titration is equivalent to 0·0015 g. of formaldehyde. The method gives satisfactory results for chrome, alum and syntan leathers, but cannot be used in the presence of vegetable tannin. Results of analyses of several commercial formaldehyde-tanned leathers are given. D. G. H.

Volumetric Determination of Hydroquinone with Potassium Dichromate. G. A. Pevcov. (*Zav. Lab.*, 1938, **7**, 110.)—In Kolthoff's determination of hydroquinone (*Rec. Trav. chim. Pays-Bas*, 1926, **45**, 745; Abst., ANALYST, 1927, **52**, 46), the end-point is considered unsatisfactory. The author states that diphenylamine sulphate is preferable to diphenylamine as indicator, but the violet of the end-point of both indicators is rapidly destroyed at 50° C. With diphenylamine sulphate as indicator, titration by the addition of an approximately $N/10$ solution of hydroquinone to standard dichromate at room temperature gives very accurate results. The method is as follows:—The hydroquinone is dissolved in water, free from oxygen, which has been acidified with approximately 50 ml. of 4 N sulphuric acid per litre. A measured volume of a standard $N/10$ solution of potassium dichromate is acidified with an equal volume of 4 N sulphuric acid, and the hydroquinone solution is run in rapidly until the solution becomes yellowish-green. A 1 per cent. solution of diphenylamine in sulphuric acid is then added (1 drop per 20 ml. of the dichromate solution being used). Further addition of hydroquinone then gives a clear green colour which rapidly becomes dirty through oxidation. As the disappearance of the colour becomes slower, the hydroquinone is added drop by drop (1 drop in 10 to 15 seconds) until the green colour remains for a long time. A 0·005 M solution of barium diphenylamine sulphate may also be used as indicator. The quinone formed is not oxidised further by the dichromate; the results, therefore, do not depend on the speed of the titration. The hydroquinone solution gives the same results if the analysis is repeated the following day. E. B. D.

Determination of Pyridine. C. Belcot. (*Ann. Chim. anal.*, 1938, **20**, 173–175.)—The methods of Schultze (*Ber.*, 1887, **20**, 3391), Spacu and Voicu (*Bull. Soc. Sc. Cluj*, 1924, **2**, 89), Spacu and Creanga (*Bull. Soc. Sc. Cluj*, 1924, **2**, 105), Malatesta and Germain (*Boll. Chim. Farm.*, 1914, **53**, 225), and François (*Compt. rend.*, 1903, **137**, 239; Abst., ANALYST, 1903, **28**, 363) were compared. Schultze's method depends on the treatment of a pyridine solution with a ferric chloride solution and subsequent titration with $N/10$ sulphuric acid until the ferric hydroxide is dissolved. The methods of Spacu and Voicu, and of Spacu and Creanga are based on the formation of the complex $[Cu(C_5H_5N)_2](SCN)_2$, that of Malatesta and Germain on the formation of the complex $[Cd(C_5H_5N)_2]Cl_2$, and that of François on the formation of a complex of pyridine chloride and gold chloride. The results obtained by the author are given in a table, from which the conclusion is drawn that for small quantities of pyridine the method of Spacu and Creanga is the best, whilst Schultze's method is satisfactory for larger quantities. The method of François is too long. E. M. P.

Inorganic

Analytical Application of Thioglycollic Acid. C. Mayr and A. Gebauer. (*Z. anal. Chem.*, 1938, **113**, 189–211.)—A solution of ferrous chloride yields with thioglycollic acid an insoluble yellow complex, $CH_2\left\langle\begin{matrix}S\\COO\end{matrix}\right\rangle Fe$, soluble in ammonia with formation of deep red ammonium ferrothioglycollate,

$Fe(SCH_2COONH_4)_2$. The reaction permits of a separation of iron from aluminium, calcium, magnesium and titanium, aluminium being precipitated as hydroxide by ammonia in presence of the soluble iron complex after previous reduction of the ferric salt with sulphur dioxide. Calcium is precipitated as oxalate from the ammoniacal solution, magnesium as ammonium magnesium phosphate. Titanium is precipitated in the same way as aluminium by ammonia, the precipitation having to be repeated once, or even twice. The iron is invariably recovered from the coloured filtrate as ferric hydroxide by heating with hydrogen peroxide. The original paper should be consulted for working details. W. R. S.

Gravimetric Determination of Zinc as Zinc Mercuric Thiocyanate. W. C. Vosburgh, G. Cooper, W. J. Clayton and H. Pfann. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 393–394.)—The method was re-investigated, the following procedure being worked out, with satisfactory results. The acid (0·1 *N*) nitrate solution, containing about 0·04 g. of zinc in 100 ml., was seeded by withdrawing a few drops and mixing with them a little of the reagent (0·1 *M* mercuric chloride solution containing a 10 per cent. excess of potassium thiocyanate), the crystalline precipitate formed being transferred to the solution, which was then slowly treated drop by drop during mechanical stirring until 0·01 to 0·02 molar with respect to excess of the reagent. After standing for an hour, the liquid was poured through a Gooch crucible, in which the precipitate was collected after two decantations with cold 0·001 molar reagent. It was then washed twice in the crucible with the same wash-liquor, dried at 105° to 110° C., and weighed as $ZnHg(CNS)_4$. The average error was 0·12 per cent. The solution may contain up to 2·5 g. of nitric, or 5 g. of sulphuric acid, larger amounts causing high results. W. R. S.

Detection of Cobalt, Copper and Ferrous Iron by β-Nitroso α-Naphthol 4-Sulphonic Acid. L. A. Sarver. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 378.)—The reagent is obtained by the action of nitrous acid upon α-naphthol 4-sulphonic acid, a 1 per cent. solution in water being used. Red, orange and green colours are given with neutral dilute cobalt, copper and ferrous salt solutions. The effect of ferrous salt can be eliminated by oxidation to ferric salt and addition of fluoride. Nickel interferes only at high concentration; hence cobalt can be detected in the presence of 1000 times as much nickel. The test is extremely sensitive, a spot test detecting about 0·01γ of metal. Nessler tubes are convenient for the work, the solution being treated with sodium acetate. The quantitative application of the reaction to colorimetric work is being investigated. W. R. S.

Complete Removal of Ferric Chloride from Solution by Continuous Extraction with Ether. S. E. Q. Ashley and W. M. Murray, jun. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 367–368.)—The main obstacle to complete removal of iron by continuous extraction with ether is the photochemical reduction of part of the ferric chloride to ferrous chloride. This is prevented if the operation is conducted in darkness or weak artificial light. The authors employ di-isopropyl ether, and use a specially-constructed apparatus, of which a diagram is given. W. R. S.

Rapid Method for the Determination of Manganese in Stainless Steel. F. W. Smith. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 360–364.)—The author eliminates chromium, which interferes with the determination of manganese, by volatilising it as chromyl chloride. One g. of steel (0·5 g. for 0·8 to 1·5 per cent. of manganese) is treated in a conical 500-ml. flask with 5 ml. of 6 *N* hydrochloric acid and 20 ml. of 70 to 72 per cent. perchloric acid. The assay is rapidly heated to dissolve the steel, the chromium being converted into chromic acid. The solution is allowed to fume for a minute after solution has taken place, when 2 to 4 g. of solid sodium chloride are added in small portions by means of a glass spoon. Two portions of salt are added after the last evolution of red fumes, the acid being boiled until the salt has been washed down by the condensing vapours. The mass is cautiously treated with 20 ml. of a mixture consisting of nitric acid (250 ml.), syrupy phosphoric acid (125 ml.), 50 per cent. sulphuric acid (185 ml.), and water (440 ml.). Boiling is continued to eliminate chlorine, which is tested for by addition of a few drops of silver nitrate solution. If chlorine is still present, boiling must be continued. When free from chlorine, the solution is treated with 10 ml. of 1 per cent. silver nitrate solution, 100 ml. of hot water, and 5 ml. of 20 per cent. ammonium persulphate solution. The liquid is boiled, and another 10 ml. of persulphate solution are added. After half a minute's boiling, the assay is quickly cooled in water and titrated with arsenite solution. A determination can be carried out in 20 to 30 minutes. The elimination of chromium is nearly quantitative (*e.g.* 18 per cent. to less than 0·06 per cent.); in many instances it is complete. This procedure for eliminating chromium was tested as to its applicability to the determination of other elements in steel. Arsenic and tin are volatilised. Selenium, titanium, aluminium and tungsten cannot be determined accurately. With phosphorus, vanadium, molybdenum, cobalt, niobium, nickel, copper, zirconium, uranium, boron, beryllium and sulphur no interference was noticed. W. R. S.

Precipitation and Determination of Vanadates. E. Carrière and H. Guiter. (*Compt. rend.*, 1937, **204**, 1339–1340; *Ann. chim. anal.*, 1938, **20**, 181.)—When vanadates are precipitated by addition of barium chloride, barium metavanadate, $Ba(VO_3)_2$, is obtained at *p*H values between 3·5 and 4·5, and a precipitate of the composition $V_2O_5.xBaO$, where x varies regularly between 1 and 3, at *p*H values of 4·5 to 10·8, whilst between *p*H 10·8 and 11·4 barium orthovanadate is precipitated quantitatively. The precipitate may contain a small quantity of barium carbonate due to the presence of sodium carbonate in the sodium hydroxide used to obtain the correct *p*H. The precipitation of vanadates by silver nitrate in an acetic acid medium of *p*H 4 to 4·6 yields the metavanadate, $AgVO_3$. When alkali or ammonium vanadate is precipitated with lead acetate in an acetic acid medium at *p*H values between 4·3 and 5, lead orthovanadate, $Pb_3(VO_4)_2$, is obtained quantitatively. E. M. P.

Colorimetric Determination of Caesium. E. S. Burksera and R. V. Feldman. (*Zav. Lab.*, 1938, **7**, 166–168.)—The caesium is precipitated with sodium silicomolybdate and the molybdenum is determined colorimetrically. *Reagents.*—(*a*) *N*/100 Caesium chloride solution. (*b*) Sodium silicomolybdate solution, to prepare which a solution of 190 g. of molybdic acid in 550 g. of water is

gradually introduced, with stirring, into a boiling solution of 33 g. of crystalline sodium silicate in 2200 ml. of water. The excess of molybdic acid, which is insoluble after boiling, is dissolved by the gradual addition of about 300 ml. of 2 *N* sodium hydroxide solution. About 200 ml. of conc. nitric acid are then added rapidly, with stirring; after impurities which are precipitated have settled out the solution is decanted and concentrated on the water-bath to 700 ml. (*c*) A 5 per cent. solution of stannous chloride. (*d*) Hydrochloric acid (sp.gr. 1·12). *Method.*—A measured quantity of the solution of caesium chloride to be analysed is added with a micro-pipette to 2 ml. of (*d*) in a centrifuge test-tube; 0·2 ml. of (*b*) are then pipetted into this. If an amount of caesium equivalent even to 0·05 ml. of *N*/100 caesium chloride solution is present an immediate turbidity is formed. After 2 minutes the solution is centrifuged, the supernatant liquid is then decanted, the precipitate is washed with 3 to 4 ml. of water and re-centrifuged, and the liquid is again decanted. The precipitate is washed into a flask with about 30 ml. of water, and 2 ml. of hydrochloric acid and 1 ml. of (*c*) are added; a blue colour (molybdenum blue) develops. When the silicomolybdate in the flask has dissolved, the precipitate adhering to the centrifuge tube is rinsed into the flask a few times with the silicomolybdate solution. The standard solution (*a*) is similarly treated, 0·1 ml. being used, and colorimetric comparison is made in a Duboscq colorimeter not more than 1 hour after the appearance of the colour. As a rapid method of determination of caesium in the alums obtained from lepidolite was required, the authors investigated a modification of the method. In this, the hydrochloric acid (*d*) was replaced by a 2·85 per cent. solution of pure alum in hydrochloric acid. Test determinations by the two methods were made on various known amounts of the caesium salt (about 0·26 to 0·8 mg.). The results obtained showed errors ranging from +5·5 to −6·3 per cent. Rubidium also forms a sparingly soluble salt with sodium silicomolybdate. Hence, in the presence of rubidium the results for caesium are too high. It is suggested that in analysing alums in which the ratio of caesium to rubidium is approximately constant, comparison solutions should be made containing caesium and rubidium chlorides in the corresponding ratio. The presence of magnesium, potassium, aluminium, calcium, ferric salts or sulphates does not interfere with the determination.

E. B. D.

Rapid Method of Determining Silicon in Aluminium and its Alloys. E. E. Gurevich. (*Zav. Lab.*, 1938, **7**, 98–99.)—A rapid modification of a standard method has been worked out. A small weight of the alloy can be used, not more than 1 hour (instead of from 3 to 3½ hours) is required for the analysis, and it is unnecessary to supervise the end of the evaporation as usual. *Method.*—The drillings (0·3 g.) are treated with "Otis-Handy" acid (100 ml. of nitric acid of sp.gr. 1·40, 300 ml. of hydrochloric acid of sp.gr. 1·19 and 600 ml. of sulphuric acid of sp.gr. 1·84) in a 150-ml. porcelain dish, 1·5 ml. of acid being added first and a further 3 ml. as the violence of the reaction subsides. The basin is covered with a clock-glass, the underside of which has been rinsed with water. When the drillings are dissolved 1·5 ml. of mixed acid (100 ml. of sulphuric acid of sp.gr. 1·84; 60 ml. of nitric acid [1: 5]) are added, the clock-glass and the sides of the dish are rinsed with hot water, and the solution is evaporated on the hot-

plate until fumes of sulphur trioxide appear. The residue left is moistened with conc. hydrochloric acid and dissolved in hot water, the solution is boiled for a few minutes, the vessel is placed on a cooler part of the hot-plate for 5 to 7 minutes, and the liquid is filtered with the aid of a pump. The precipitate is washed five times with hot water to free it from chlorides (further washing yields too low results), ignited, weighed and treated with hydrofluoric acid as usual. In test experiments with various alloys containing about 0·6 per cent. of silicon the differences between the results obtained by the standard method and by the rapid method ranged from —0·02 to +0·02 per cent. Berl–Lunge has stated that evaporation at too high temperatures may lead to some volatilisation of silicon hydride (*cf.* Callendar, ANALYST, 1933, **58**, 81), but the author found that with temperatures of evaporation higher than in the standard method the same results were obtained. E. B. D.

Microchemical

Automatic Regulation of Combustions. H. Reihlen. (*Mikrochem.*, 1937 38, **23**, 285–301.)—In a micro-determination of carbon and hydrogen the sample is burned slowly by moving a burner gradually along the combustion tube towards the boat containing the sample. This usually takes 10 to 15 minutes, and the boat is then heated with the burner stationary until the whole combustion has taken 25 minutes. An automatic device, which can be set differently for volatile and non-volatile substances, requires no attention throughout the whole combustion. An alarum goes off at the end of 25 or 30 minutes, according to the volatility of the sample. The speed is controlled by the oxygen pressure, so that the combustion is carried out at exactly the correct speed better than by personal control. Two types of automatic regulators are made, for micro- (2–5 mg.) and for semi-micro combustions (20–50 mg.). Instead of the usual oxidising filling in the combustion tube (lead chromate and copper oxide), Vinonite B is used. This is a mixed catalyst with copper oxide as basis and consisting of copper, lead, chromium, manganese and silver in the atomic proportions 12: 3: 3: 1: 1. Freshly-filled tubes must be heated to 600–700° C. for 3 to 4 hours in a stream of oxygen before use. For the absorption of water half phosphorus pentoxide and half magnesium perchlorate are used, so that the gases pass first through the magnesium perchlorate and then through the phosphorus pentoxide. Ascarite is used for the absorption of carbon dioxide. Flaschenträger absorption tubes are preferred; these are weighed full of oxygen against similar tubes as tares. As accurate results are obtainable with the automatic as with hand control, both on the micro- and semi-micro scale. The semi-micro combustion apparatus is cheaper, as a micro-balance is unnecessary. The apparatus is obtainable from E. Bühler, Tübingen. J. W. M.

Semi-Quantitative Spot Tests. H. Yagoda. (*Mikrochem.*, 1938, **24**, 117.)—The amount of test substance present may be estimated when the comparative spot tests are confined to equal areas. Paper or other absorptive material is impregnated with a water-resistant substance such as wax, paraffin wax, cellulose ester or natural or synthetic resin (Bakelite). Paraffin wax rings are made in

filter-paper by first dipping thin tissue paper in melted paraffin wax at 100° C., draining, cooling to room temperature and placing it on the filter-paper. Paraffin wax rings can then be stamped on the filter-paper by means of a bronze hollow cylindrical stamp of the required internal diameter to give a reaction field 100 sq. mm. in area (or for traces 50 or 10 sq. mm.), the outer diameter for each size being 20 mm. The stamp is heated to about 90° C. and pressed for a moment on the paraffin paper. The paper is impregnated with reagent immediately before use by placing it on a small flat-topped funnel attached to a filter-flask, and holding it firmly in position by means of a small metal ring. The required amount of reagent solution is added, drop by drop, and allowed to evaporate; a measured volume of the test solution is added. As soon as the reaction is complete mouth suction is applied to the suction flask, excess liquid collects on the underside of the filter-paper and is removed with strips of filter-paper or with small capillary tubes, and finally by placing the test-paper on a dry filter-paper and drying it at 60–90° C. When the reaction product will not resist heat the test-paper is washed with alcohol and dried at room temperature. The colour of the paper is then compared with that given by standard amounts of the test substance. *Reagents.*—The reagent must always be present in large excess; for an area of 100 sq. mm. 1 mg. of reagent is used for 20 γ of test metal; methyl alcohol is usually preferable to ethyl alcohol, being more volatile, and as the reagents are usually more soluble in methyl alcohol, a smaller volume is required to give the correct concentration. The method is applicable to the estimation of aluminium, arsenic, bismuth, cobalt, copper, iron, nickel, and silver. For *aluminium* the alizarin test is used; *arsenic* is estimated by development of arsine which then reacts with mercury bromide; for *bismuth* the cinchonine test is used, for *cobalt* the benzimidazole test; for *copper* the benzoin oxime test; for *iron* either the Prussian blue or the $\alpha\alpha'$-dipyridyl test; for *nickel* the dimethyl glyoxime test and for *silver* the dichromate test. Tests may sometimes be carried out on glass within rings of paraffin wax or other material. The procedure is applicable to amounts varying from 0·1 to 250γ of the test ion. J. W. M.

Collected References: Applications of Micro-Technique in Food Analysis. W. Diemair and G. Herrmann-Tross. (*Mikrochimica Acta*, 1937, 2, 333–342.)—References and brief summaries of micro methods used in the analysis of foods are given as follows:—proteins and amino acids (11 references), fats (7 references), lipoid phosphorus (1 reference), cholesterol (2 references), carbohydrates (11 references), organic acids (4 references), sulphurous acid (3 references), metals and non-metals (31 references), other substances including vitamins (16 references). J. W. M.

Reviews

ORGANIC CHEMISTRY—AN ADVANCED TREATISE. H. GILMAN. Two volumes. Pp. 1890 + lvi (index). New York: Wiley & Sons; London: Chapman & Hall. 1938. Price 37s. 6d. each volume.

This is a collaborative work by specialists; as stated in the preface "Each author was asked to prepare a chapter dealing with a subject of particular interest to himself. It was hoped to obtain, in this way, an authoritative treatise which would cover most of the important phases of organic chemistry."

The only criticism that the reviewer can make of this most useful work concerns its title, which may be rather misleading: these books do not constitute a textbook or systematic treatise in the usual sense but rather a collection of monographs dealing with separate topics. Some of these monographs—or chapters—are of considerable length; that dealing with stereoisomerism, for example, occupies over 250 pages, and the one concerned with molecular re-arrangements runs to 180 pages.

This minor criticism will lose its point, however, if the intentions of the editor are realised, for, as stated in the preface, "It is planned to revise both volumes at intervals, not only in order to bring the present material up to date, but also to permit the inclusion of new chapters to fill the more conspicuous gaps."

The topics have, for the most part, been chosen because of their intrinsic importance (*e.g.* open-chain nitrogen compounds; alkaloids) or of their current interest (*e.g.* carbohydrates; electronic concepts of valence) or because the subject dealt with is in a state of rapid development (*e.g.* sterols and related compounds; the significance of resonance), and are dealt with by workers who have been actively engaged in the subjects of which they treat.

The editorial board deserves the thanks of chemists for the great care and labour necessarily involved in the production of these two fine volumes; they constitute a real achievement of united effort.

Now that the editors have got so well into their stride it may be hoped that in the not-too-remote future they will produce a companion volume; may it contain a treatment of the subject of the Walden Inversion more commensurate with its importance than the five pages now allotted to it.

The value of the work is enhanced by the provision of a detailed index, copious references to recent original literature and numerous cross references between the different chapters.

J. KENYON

QUALITATIVE ANALYSIS BY SPOT TESTS. By F. FEIGL, Ph.D. Translated by JANET W. MATTHEWS, Ph.D., F.I.C. Pp. 400, with 24 Illustrations. Amsterdam: Nordemann Publishing Co. British Agents, Imperia Book Co., 26 Bloomsbury Street, W.C.1. 1937. Price 30s.

Many chemists in this country are already familiar with Professor Feigl's "*Qualitative Analyse mit Hilfe von Tüpfelreaktionen*," the second edition of which was reviewed in the ANALYST (1935, **60**, 205), and its value has been greatly appreciated in many quarters. In order to make the volume available to a wider

circle of readers Dr. Matthews has undertaken the task of translating this production into English, thereby also rendering it more acceptable even to those well acquainted with the German language. This translation is confined to the practical portion of its progenitor, with additional subject-matter that has been elaborated since it was published, and it is intended that the theoretical part shall be issued at a later date.

Those unacquainted with the earlier German editions may gather some idea of the scope of the volume from the following summary of its contents. After a few general remarks on micro spot methods, descriptions are given of various simple pieces of apparatus used in this work, these being succeeded by the reactions for traces of the commoner and rare metals and for inorganic acids. The next section well illustrates the value of spot tests in the analysis of mixtures containing compounds and alloys of metals and gives in detail four tables elaborated by different chemists for this purpose. Section VI deals with the reactions for aliphatic and aromatic organic substances, including the detection of elements, radicals and specific compounds. The text concludes with a wide selection of reactions for the detection of impurities, and so forth, in water, minerals and numerous industrial products, and an excellent series of tests for the identification of dyes both in the free state and on textile materials. Throughout the volume a description is given of the principle underlying each new test described, the method by which it is carried out, the minimum limits of identification and concentration, the composition of the reagents used and (what is particularly valuable) a brief list of interfering substances, if any, and means by which their effects may be nullified.

The final pages of the volume contain a tabular summary of the reactions described in the text (which would have been of greater utility had the items been arranged in alphabetical order) and the usual name and subject indexes. There is considerable evidence that the subject-index was compiled by someone unfamiliar with the subject-matter of the volume (and the reviewer has since ascertained that this was the fact), and as a result this index is less satisfactory than its importance merits. Such bald entries as "Heller's procedure," "Aniline, use in analysis," "Eosin," etc., are of little value unless further details are given. Some prominent text items are missing and cross-indexing is incomplete, whilst in a few cases the page numbers are incorrectly given. A sheet bearing four corrections was inserted in the volume, but a few additional ones were encountered in the text: thus on pp. ix and 361 "animal" occurs instead of "aniline" in connection with dyes; reference is made on p. 3 to the "soldering" of platinum loops, but no mention is made that pure gold must be used for this purpose and not ordinary solders; on pp. 323 and 324 the use of ammonium mercury silver thiocyanate reagent is mentioned and reference is given to its preparation on p. 45, but on turning to this page no indication of silver in its composition is given. Notwithstanding these minor defects, which will no doubt be eliminated in a future edition, the book is a valuable production giving all essential details with a completeness seldom met with; it is well worthy of a place in the library of every analytical chemist. Its production reflects considerable credit on the translator for the successful manner in which she has rendered available to English readers much original work of rapidly increasing importance at the present time. T. J. WARD

ANALYTICAL CHEMISTRY—VOL. I—QUALITATIVE ANALYSIS. Based on the German Text of F. P. TREADWELL. Translated and Revised by W. T. HALL. Ninth English Edition. Pp. x + 630. Chapman & Hall. 1937. Price 22s. 6d.

With the changing years textbooks are bound to change as edition follows edition, but with a book so excellent and proved as "Treadwell" it is a matter of congratulation that the change has not been too drastic. Of the alterations, some seem definitely valuable, some a matter for regret. Part I, dealing with the basic principles of analytical chemistry, has been largely rewritten; the result is admirable, especially the section on colloids, which might with advantage have been considerably expanded. In Part II the order of presentation has been changed, so that it now begins with silver and ends with the alkalis, following the order of the qualitative table; this seems a sensible alteration. A modification that does not seem so happy is the omission from this edition of Noyes and Bray's comprehensive scheme for the detection of rare and common elements. As time goes by more and more elements are brought into industry and so may be encountered in the most unlikely situations; when so encountered some of them are likely to upset badly the scheme of analysis of the old table. The authority of the old qualitative table rests largely on tradition, and perhaps even more on inertia, and there seems in these days no justification for the exclusion from our chemical consciousness of, say, tungsten, molybdenum, vanadium, thallium, zirconium and many more, to say nothing of the platinum we are all liable to meet as a contaminant due to fusions in platinum dishes. The reason given for the omission is that "the procedure is so long that few students find time to follow it throughout." This touches the root of a matter fundamental to assessing the value of the book to the practising chemist; it is essentially a student's textbook, and that not merely (possibly not principally) as a guide to analytical chemistry but as an integral part of his chemical training; hence the numerous explanations of reactions in terms of physical chemistry. This orientation may seem a matter of indifference, facts being facts and chemistry being one and indivisible, but the physico-chemical explanation of a fact may lead to deductions (from which perhaps the assumption is that students are immune), and if perchance the "explanation" is not so much an explanation as a convenient illustration of a chemical theory or if the "fact" is not quite so much a fact as has been assumed, these deductions are apt to go wildly astray. An example of physico-chemical zeal outrunning analytical discretion is to be found on p. 51, where it is shown that, calculating from the solubility products, the separation of copper sulphide from zinc sulphide should be practically complete in 0·3 N acid. This demonstration suffers from two drawbacks:—(*a*) it is not true—at any rate in the rigid quantitative sense implied; (*b*) it ignores Glixelli's work, which showed that a large proportion of the zinc in a solution of zinc sulphate in 2 N acid is precipitated by hydrogen sulphide if left over a period of months.

The rarer elements are by no means neglected; all are touched on, if only descriptively, in Part V, which covers 100 pages, but they are isolated in an aristocracy of their own and their relationships with the common herd are by no means apparent. In a book of this size and complexity there are bound to be

mistakes, but considering the vast amount of information accumulated these seem relatively few. Sections vary considerably in this respect; that on the Marsh and Reinsch tests seems unusually unfortunate. One would gather that neither acid nor chlorides are essential to the Reinsch test for arsenic (p. 156; antimony is not mentioned as giving the test); that hydrochloric is the best acid to use in the Reinsch test for mercury (p. 108) but is positively deleterious to the Marsh test for arsenic (pp. 151 and 153); also that "all compounds containing arsenic" give the Marsh test. The section on hypophosphorous acid also leaves something to be desired; of the three metals whose salts are stated to be reduced to metal (p. 363) the reduction of gold and mercury is so easy that it cannot be regarded as in any way characteristic, while that of copper depends on the nature and strength of the acid used; the characteristic reaction with arsenic and the reduction of sulphur dioxide are not mentioned. The inference that barium carbonate does not precipitate iron in the cold (p. 576) is decidedly misleading; also, it is not true to say (p. 312) "potassium dichromate in the presence of dilute sulphuric acid does not cause separation of bromine from aqueous solutions of bromides." If mistakes are relatively unimportant, however, the same cannot be said of proof-reading errors, the proportion of which is a great deal too high. The following are among those noted:—p. 122. "The trivial name dithizone has been proposed for *diphenylcarbazone*." This statement leaves in doubt what is intended every time "dithizone" is mentioned in the book; p. 127, "sulphate" for "chromate"; p. 344, "mercuric" for "mercurous"; p. 392, "phosphates" for "phosphites"; p. 428, "perchlorate" for "persulphate" (several times); p. 578, m.p. of gallium 301° for 30°.

The book as a whole, however, remains the excellent textbook (especially from a teaching point of view) that we have known for so long. Many of the new organic reagents for metals, now coming to light in such numbers, find a place in this edition; the directions for their use are, in the main, admirable, but the unfortunate error referred to above leaves it entirely uncertain in many instances whether diphenylcarbazone or diphenylthiocarbazone is intended, as both compounds give colours with a number of metals. The descriptive sections at the head of each element have been amplified and are among the best features of the book. Considerable economy of space could be effected (thus eliminating one reason advanced for the non-inclusion of Noyes and Bray's table), by condensing into tabular form all those reactions which are not really characteristic of the acids and bases concerned; many of those given under the headings of separate radicles are really group reactions. The kindly and friendly spirit that somehow seems to emerge from the pages is rare indeed in textbooks of this description and lightens the labour of understanding difficult passages. Such warnings, too, as "frequently a little chloride gets into the nitric acid bottle from careless interchange of stoppers" (p. 503) are unusual, but likely to save the unwary student much searching of heart. If, however, a student has worked up to p. 501 without discovering what sulphur dioxide and hydrogen sulphide smell like, he must have been unobservant indeed. Sometimes Homer nods, and one gets statements such as "thallium chloroplatinate which is *quite insoluble* in water, 1 part dissolves in 15,600 parts of water at 15° and 1950 parts at 100°" (p. 574), which somehow

seem unworthy of the precise physical chemistry of earlier pages. It is a book which, apart from the proof-reading slips, some of which are serious, continues to live up to the deservedly high reputation it has acquired as a training ground for students. Printing and binding are of the same high order as those of Vol. II (*cf.* ANALYST, 1937, **62**, 234). B. S. EVANS

HANDBUCH DER LEBENSMITTEL-CHEMIE. Vol. VII. Alkoholische Genussmittel. A. BÖMER, A. JUCKENACK and J. TILLMANS. Pp. 828. Berlin: Julius Springer. 1938. Price RM.99.

The seventh volume of this monumental handbook, started by Bömer, Juckenack and Tillmans, is now continued under the editorship of Juckenack, Bames, Bleyer and Grossfeld. The present volume, which deals with alcoholic beverages of all kinds, is edited by Dr. Bleyer. The names of its editor and contributors afford some indication of its quality.

The treatment of the subject differs somewhat from that of most English textbooks, since it includes much more detail of manufacture and processes than is to be found in most such books. Perhaps one might say that the work is teutonically thorough as well as thoroughly teutonic. First there is a description of the history, morphology and chemistry of yeast and a brief but good survey of the theory of fermentation, before Drs. Bleyer and Diemair enter on a detailed description of the materials and methods of brewing. Each substance used and each operation is studied in some detail; then comes a careful account of methods of analysis applicable not only to beer but to all kinds of brewers' materials. Finally, there is a bibliography and some twenty pages of German law relating to beer; how complicated is German law compared with ours!

The major item in the book is "Wine," written by Dr. Vogt, and occupying about 280 pages, followed by 80 pages on law relating to wine. The chapter on wine is the most comprehensive with which the reviewer is acquainted and gives both statistical and analytical details covering an unusually large number of constituents. It is particularly useful to have so much concise information as to the usual and limiting quantities of the less well-known constituents. One result will be that the detection of spurious or falsely described wines will often be more practicable; for, although, as the authors state, there are no specific tests which enable this to be done, the skilled palate fortified by more detailed statistics for the particular wine goes far to solve a problem otherwise insoluble.

The section on "Spirits" is contributed by Professor Buttner; it deals particularly with brandy and also with whisky, rum, gin and almost all varieties of liqueurs. Then follows a chapter on law relating to alcoholic beverages in all the principal countries. In this connection one notes that while German law on wines requires about eighty pages and that on spirits forty pages, English law on alcoholic beverages requires but a quarter page. The intricacies of proof spirit and the general provisions of the Food and Drugs (Adulteration) Act have escaped notice.

The accuracy and thoroughness of the work as a whole well maintains the standard of the earlier volumes and compels admiration. There is no doubt that the chemical study of wines and spirits has been more intensive in Germany

than in England. The literature of the subject has been well surveyed, though we notice a few omissions, such as that of Monier-Williams's method for benzoic acid (perhaps the Reports of our Ministry of Health are not adequately noticed in the German journals) and the alizarine-zirconium method for fluoride. These, however, are but minor matters and do not detract from the general excellence of a work which is undoubtedly the most encyclopædic treatise on food chemistry of recent times.

H. E. Cox

CEMETERIES OF ARMANT I. By Sir ROBERT MOND, LL.D., OLIVER H. MYERS and OTHERS. Large 8vo, 2 vols. Vol. I, *The Text*, Pp. 300; Vol. II, *The Plates*. Egypt Exploration Society, Manchester Square, London, W.1. 1938. Price 25s.

The excavation of the cemeteries, dating from Predynastic times upwards, on the edge of the desert to the west of Armant yielded no spectacular finds or startlingly new historic facts. Yet the results have brought to light many details of great interest and are of far-reaching importance. The aim of the modern archæologist is to extract the utmost possible information from all the material available, and material of no outstanding intrinsic value is now made to yield information many times more valuable than that given by more spectacular discoveries.

This is due to the assistance of experts in the study and interpretation of the collected data and to the application of statistical methods. The advice of the expert has been sought wherever it could be of value, and the long list of 46 competent scientists consulted included representatives of many branches of science. All the resources of modern science have been brought to bear on the problems. The statistical method yields results that are cumulative. Every single object found or purchased on the site has been listed in registers for ready reference.

Of outstanding interest was the discovery of pottery fragments—remains of a culture which can be traced at intervals across the Sahara to a point further west than Timbuctoo. If the pottery can be dated, a starting-point might be given to the chronology of the Sahara, a subject bound up with problems of climatic changes and movements of the world ice-caps. "It is no exaggeration to say that these few hundred small broken sherds may ultimately transcend in importance any other single find in Egypt."

As a result of using some of the Predynastic jars to contain water, a new method of removing incrusted salts was discovered. The action of the water seeping through the pottery removed the impurities far more rapidly than if the pots had been left soaking in water. By standing the weighted pots, empty of water, in a bowl filled with water to the level of the brim of the pot, all the salts were removed after three soakings. A very slight amount of grease was found sufficient to make the pots non-porous for all practical purposes, and this method may have been employed in ancient times, as it is to-day by the Masai.

The material and methods of manufacture of beads have been exhaustively studied. They show a wide range of materials, including green and yellow fluorspar, wood opal, serpentine, beetle femora and thoraces, glass, glazed cornelian,

amber and bitumen. Determinations of specific gravity and refractive index were made, and Bannister's Composition Charts were utilised as well as Ostwald's Colour Album. A fortunate find in connection with the study of abrasives was a firmly adhering coating in a dead-hole in a steatite bead. This proved to be crushed chert or flint. Spectrographic examinations and photomicrographs of other specimens were made. A modification of Reutter's methods was used in the investigation of the material of the resin beads.

Attempts were made to gauge the original reflective power of a mirror of Middle Kingdom date after cleaning and polishing, but it was found difficult to remove entirely the products of corrosion. One side of the mirror was slightly concave and the other slightly convex.

The painted gesso* objects (described as the most interesting find of the season's work) were the subject of special study. The presence of well-preserved foraminifera pointed to a method of manufacture by a process of "hydraulicking,"† rendering kilning unnecessary.

A Predynastic skeleton with eunuchoid characteristics and a skin garment presented features of unusual interest. The latter showed seams sewn with astonishingly fine needles corresponding to modern sizes 8 to 10.

A point which might be adopted with advantage by all archaeologists is the use of the German word *Fundplatz* instead of the ambiguous *provenance*, which might refer to the original as well as to any subsequent location of an object.

The report has involved an enormous amount of time and labour and the authors have clearly spared no pains to make these volumes a valuable source of reference for future workers. Vol. II is devoted entirely to the plates, which are reproduced in excellent style. R. W. SLOLEY

THE CHEMICAL ANALYSIS OF FOODS. By H. E. COX, Ph.D., D.Sc., F.I.C. Second Edition. Pp. ix + 329. London: J. & A. Churchill. 1938. Price 21s.

Appreciation of this unassuming book increases as acquaintance progresses. Its author has set out, as the sub-title indicates, to produce a practical treatise, and his wide experience enables him to write nearly all the time from his own knowledge. By indications throughout of his own choice of alternative methods and by such touches as "a specially designed apparatus which is rather prone to fracture" he does succeed in passing on some of the results of this experience, and this is refreshing in face of the increasing tendency in so-called practical text-books to describe half a dozen methods and leave the reader the choice of trying them all for himself or of picking one out haphazard.

A comparison of the present volume with the first edition and the review thereon (ANALYST, 1926, **51**, 164) shows that the author has attempted to deal with most of the criticism made at that time, and indeed, to the writer, only one serious defect now remains among those then noticed, and that is the allocation

* A term applied by Egyptologists to plaster made of whiting and glue.

† Limestone containing only a small percentage of clay-body (hydrated aluminous silicate) has hydraulicking properties, that is to say, if heated to drive off a portion of water, the residue reduced to powder will re-set on moistening. Thus kilning to the temperature required to produce quicklime may not have been necessary.

of the available space to the various parts of the subject-matter. Oils and fats, other than butter and margarine, for instance, still receive but twenty pages—under 7 per cent. of the total. This, no doubt, is a defect of the book's principal virtue derived from the author's intention to discuss as far as possible only those methods of which he himself has experience, and in compensation the space allotted to sugars, cereals, fruits and spices is perhaps larger than the size of the book warrants.

Among criticism of details may be mentioned the values given for the specific rotations of the common sugars at 20° C., which differ considerably from those usually accepted, the use of the phrase "polarimeter" instead of "polarised light" (p. 55), the omission of any reference to parasites under cereal foods, or to the possibility of foods containing hydrogen cyanide or ethylene oxide as a result of fumigation. Under eggs, the various methods of preservation deserve attention, as does the use of ultra-violet light in detecting the removal of marks of origin. The useful description of several methods for the estimation of tannin in tea would have been rendered more valuable by a table showing the results obtained by each process upon the same sample. The uninitiated reader of the chapter upon alcoholic liquids would not be able properly to distinguish between sweet and dry wine nor between mild and bitter beer; in the same chapter there are several references to silent spirit, a substance nowhere described in the text. The upper limit of 2 grains of tin per pound in foods is quoted, but there is no indication of what amounts of lead, copper or zinc should be allowed, though methods are given for the determination of traces of these elements. Illipé fat is still ignored in connection with cocoa and chocolate. The statement that sweetened condensed milk "abounds in bacteria" would be somewhat alarming if it were generally true. In dealing with the phosphatase test, the short test only is described, and the deduction that "if only a faint blue colour develops in all four tubes the milk has been heated but not properly pasteurised" is incorrect.

In the new edition the section on sugars now includes the Lane and Eynon method, and the sections on jams, meat and fish products, milk, eggs, infant foods and some food fats have been expanded. The titration of ascorbic acid is described and considerable attention is devoted to preservatives and traces of metallic elements. In spite of this, there are but six more pages in the new edition; each page, however, contains an additional two lines of print. The book is well produced, of convenient size and fairly well indexed.

The tests selected are well described and are in every instance all that would be required to decide whether a sample was satisfactory under the Food and Drugs Act, but with few exceptions are not sufficient to settle the more difficult question of quality. Perhaps this must always be left to more specialised monographs. The author does something in this cause by judicious references to the literature, which are sensibly given in parentheses in the context, and not at the end of the chapter or book. The references, too, are nearly all readily available to English readers.

Considered as a whole, the book is a reliable guide to the laboratory work necessary in the general chemical examination of foods. H. E. MONK

RECENT ADVANCES IN VOLUMETRIC CHEMICAL ANALYSIS. By H. B. KELLOG. Pp. vi + 208. Philadelphia: Lefax, Inc. 1938. Price, paper cover, $2.00; ring binder, $3.00.

This compilation of recent contributions to the advancement of volumetric analysis is put together on the loose-leaf system. It consists, for the most part, of reprints and translations of selected work published during the last ten years. Most, but not all, of the original sources are acknowledged in either the preface, the text, or the bibliography that follows each article. The monographs of the Institute of Chemistry, The British Drug Houses, Ltd., The G. Frederick Smith Chemical Co., U.S.A., and "Modern Methods in Quantitative Chemical Analysis," by A. D. Mitchell and A. M. Ward, have been largely drawn upon; other sources are mainly the periodical literature of America, England and Germany, with *Ind. Eng. Chem., Anal. Ed.*, *Z. anal. Chem.*, and *J. Amer. Chem. Soc.* predominating. There are five references to original papers published in THE ANALYST, in addition to those contained in bibliographies attached to reprints of monographs.

The type, though small, is easily legible. A special feature is a list of the necessary reagents for each method of analysis described. The style, though excellent in parts, is as varied as the sources of the information.

The basis of selection of material for inclusion was the proved reliability of the methods described, and the mode of presentation such as would afford sufficient detail to enable it to be followed in the laboratory. In these objects, the compiler would appear to have been successful. Moreover, he has succeeded in dealing with no fewer than forty-seven elements and compounds in a compact space; and chemists who desire a large amount of recent information concentrated in a small bulk, such as those whose work takes them out of reach of reference libraries, will find this publication of practical value.

As the subject matter is arranged alphabetically and the pages numbered consecutively, the reviewer finds it difficult to decide whether the work is intended to be regarded as a collection of data sheets or a book. Since the separate articles over-run numbered pages, to which an index is provided, it would appear that it is intended to be looked upon as a book. If so, the advantages of the loose-leaf system are largely lost; a permanent binding would have been preferable. If, on the other hand, it is intended to form part of a loose-leaf system of note keeping, there should have been no over-running of pages between articles; alphabetical arrangement, with a subject heading at the top of each page, would have been sufficient. In the reviewer's opinion, the latter course would have been the better arrangement, and would have avoided difficulties in compilation, such as have led to inclusion in the body of the work of articles on "Std. Solutions and Preparation" and "Volumetric Factors," which would have been better placed together, and at the end. A whole-hearted devotion to the loose-leaf system would, in addition, afford other advantages to a work of this nature; not least amongst which would be: (1) facilitation of additions necessitated by still more "recent" advances, (2) revision of parts, without the necessity for reprinting the whole, and (3) correction of errors by the issue of supplementary pages.

A careful reading of the work has revealed some slips, of which the following may be mentioned, as likely to mislead a reader. In the equation on p. 152, "2I" should read "$2I_2$." On p. 40, near bottom, there is an error in transcription from A. D. Mitchell's "New Indicators and Other Reagents employed in Volumetric Analysis"; for "nitrate" read "nitrite." In the account of Dr. B. S. Evans's method for determining small quantities of antimony in lead and its alloys, on p. 58, the interpolated word "to" in line 8 of the sub-section, creates ambiguity and requires deletion. On p. 15, line 20 from the bottom, the word "from" has been missed in the B.D.H. monograph on "Adsorption Indicators" by A. W. Wellings. Obvious printers' errors are to be found on pp. 32, 63, 107 and 141. There is also an error on p. 60, where "aluminium" should read "antimony." F. L. OKELL

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