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Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXXI. The Determination of Tungsten in Earth-Acid Minerals

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(WORK DONE UNDER THE SOCIETY'S ANALYTICAL INVESTIGATION SCHEME)

THIS Section concludes our study of the determination of tungsten as part of the analysis of earth-acid minerals by the tartaric acid method. It may be regarded as continuing Section XXVI,[1] which reached the conclusion that "we cannot yet assign to tungsten a definite position in our proposed analytical scheme," as its precipitation in the procedures studied was incomplete. Having meanwhile elaborated methods for separating tungsten from the earth acids and associated earths,[2] we still required a procedure for recovering it from the tartrate solution of the mineral. What we have been able to achieve in that direction is given in the present paper.

A. PRINCIPLE OF THE METHOD.—It has been shown in Section XXVI[1] that the major fraction of the tungstic acid is precipitated with the earth acids by tartaric hydrolysis. In the light of our subsequent experience, this procedure is probably the only means of recovering the bulk of the tungsten from tartrate solution, the hydrolysis precipitate, *HP*, being treated by the magnesia method[2] for the separation of the tungsten from the crude earth acids. Exps. 1 and 2 of the earlier Section are reproduced below.

	G taken				Used	
Exp.	M_2O_5	WO_3	*HP*	WO_3 in *HP*	$KHSO_4$	$C_4H_6O_6$
	g.	g.	g.	g.	g.	g.
1	0·1510	0·0148	0·1623	0·0127	3	3
2	0·1507	0·0150	0·1584	0·0107	4	6

It should be recorded, in view of what follows, that the pentoxides used contained 61·4 per cent. of tantalic and 38·6 per cent. of niobic oxide, and that the precipitation of *HP* took place in a bulk of 250 to 300 ml., 30 ml. of strong hydrochloric acid being used as precipitant. The results show that the recovery is adversely affected by an increase in the bisulphate and tartaric acid.

Our next problem was the recovery of the minor tungsten fraction not precipitated by tartaric hydrolysis. Several procedures were evolved, and tried with indifferent success. We will confine ourselves to a brief description of two of our schemes, *viz.* induced ammonia precipitation and double tartaric hydrolysis. These will be followed by an outline of the method we propose to adopt in the analysis of earth-acid minerals and our recommendations for the use of a correction factor, supported by the results of test analyses.

B. Induced Ammonia Precipitation.—For the analysis of complex earth-acid minerals by the tartaric-acid method, we intend following the process previously described for the analysis of tantalite as far as the stage at which the sulphides of iron and manganese have been precipitated (XXVII, stage d^3). Thereafter the tartaric acid is no longer required for keeping the remaining earths in solution; rather does it complicate their separation.[4] We therefore proceed by destroying the tartaric acid[5] in the filtrate from the sulphides and converting the residual acid mass by evaporation into the original bisulphate melt, which is dissolved in water. The clear, or almost clear, solution is treated with 5 g. of ammonium chloride, heated to boiling, and precipitated with a slight excess of ammonia. The dioxide earths, earth acids (minor fraction), rare earths, uranium, aluminium, and beryllium are thus precipitated, while the alkaline earths pass into the filtrate.

Now it has been observed that ferric hydroxide precipitated by ammonia acts as a collector of small quantities of tungstic acid. Hillebrand and Lundell[6] state that "tungsten can be gathered, when present in minute amount, by adding an excess of ferric salt and precipitating with ammonium hydroxide." It occurred to us that other hydroxide precipitates might act like ferric hydroxide—an assumption which was verified in Exps. 3 to 8. In each of these the mixed oxides were fused with potassium bisulphate (4 g.), and the product was dissolved in 250 ml. of water. The solution was treated with ammonium chloride (5 g.), heated to boiling, and treated with a slight excess of ammonia. The precipitate was ignited in a platinum crucible and assayed for tungsten by the magnesia method.

Exp.	Taken		WO_3 Recovered	WO_3 Error
	WO_3	Collector		
	g.	g.	g.	g.
3	0·0034	Fe_2O_3 0·2057	0·0034	0·0000
4	0·0030	do. 0·0553	0·0026	−0·0004
5	0·0032	TiO_2 0·2041	0·0028	−0·0004
6	0·0040	U_3O_8 0·2046	0·0026*	−0·0014
7	0·0039	Y_2O_3 0·2037	0·0026	−0·0013
8	0·0048	Al_2O_3 0·2028	0·0020	−0·0028

* In the magnesia method, part of the uranium follows the tungsten into the alkaline filtrate. Both metals give a brown tannin precipitate, the uranium complex dissolving readily when the liquid is acidified prior to the addition of cinchonine solution. When the tungsten precipitate has been filtered off, the uranium may be recovered from the filtrate by ammonia precipitation.

The results show that iron and titanium are good collectors, the others being indifferent or poor ones. Only in Exp. 8 were we able to detect tungsten in the ammoniacal filtrate by the cinchonine test described under G, Exp. 23.

C. DOUBLE TARTARIC HYDROLYSIS.—Precipitation of tungstic acid having proved fairly efficient in presence of preponderating quantities of earth acid, we argued that a repetition of the process would recover all but traces of the minor tungsten fraction. We proceeded as follows: the first hydrolysis precipitate, HP^1, was treated by the magnesia method, yielding a precipitate, MP, consisting of the tungsten-free earth acids, and a filtrate from which the major tungsten fraction was recovered by precipitation with tannin and cinchonine. The filtrate from HP^1 was boiled down with sulphuric and nitric acids for the destruction of the tartaric acid. The liquid was transferred to a silica crucible and converted by evaporation into the original bisulphate melt, with which the ignited MP was fused. The product was dissolved in tartaric acid, and the solution was again hydrolysed, the precipitate HP^2 being treated as HP^1 for the recovery of the minor tungsten fraction.

D. AUTHORS' PROPOSED METHOD.—We carried out more than 20 experiments, using the above processes with and without modifications; in the ammonia method (B) a variety of collectors (single and mixed) was tried. The total tungstic-oxide recoveries were found to be attended with negative errors, varying from less than 1 mg. to more than 2 mg. on a quantity of about 15 mg., adopted in our tests as representing the recorded maximum content in 0·5 g. of earth-acid mineral. Without going into tedious experimental details, we may say that we found this investigation at least as arduous as any of the preceding ones, the last mg. or two of tungstic oxide eluding all our efforts at recovery.

We therefore decided on a fresh series of tests, in which a maximum recovery of the major tungsten fraction was to be attempted. If that was accomplished, we argued that it would hardly be worth while doing a disproportionate amount of work, and perhaps vitiating the determination of the remaining constituents, for the sake of an incomplete recovery of the minor tungsten fraction. The amount of the latter might be estimated more closely by computation on the basis of our observations.

The new tests proved more successful. The recovery of the major tungsten fraction improved on the whole, thanks to standardised conditions of precipitation at higher concentration.[7] Another important result, however, was our observation that tantalic oxide induces almost quantitative precipitation of tungstic oxide, whereas niobic oxide (which is itself less completely precipitated) collects tungstic oxide less effectively than does tantalic oxide. If tantalic oxide preponderates over niobic oxide, the tungsten recovery is satisfactory; if the reverse is the case, it is lower. If, however, the amount of tungsten present is very small, there appears to be no marked difference in the collecting power of the two earth acids (see Exps. 21 and 22). In this connection it should be mentioned that the earth acids precipitated by tartaric hydrolysis differ from each other in appearance: tantalic acid is a sub-translucent, flocculent precipitate which settles readily, leaving the supernatant liquid perfectly clear; niobic acid is white and opaque, flocculates less readily and, after settling, leaves the liquid more or less milky.

Procedure (*Major Tungsten Fraction*).—The mixed oxides (0·2 to 0·25 g.) are fused with potassium bisulphate (3 g.), and the melt is dissolved in a hot solution of tartaric acid (3 g.).[8] The clear solution, diluted to 150 ml., is treated while boiling with strong hydrochloric acid (25 ml.), boiled for 3 minutes, and left to settle for a short time. If still cloudy, the supernatant liquid may be treated with a little tannin, which is superficially adsorbed and thus promotes flocculation. In any case, the precipitate is thoroughly mixed with filter pulp, collected, returned to the beaker for washing, etc., as usual.[9] It is ignited in a platinum crucible and fused with potassium carbonate for the determination of the tungsten by the magnesia method.[2] The tannin-cinchonine precipitate is ignited at a low temperature in a tared porcelain crucible and weighed.

Purification.—The yellow colour of the weighed oxide is a good indication of its purity. If the niobium content of the mixture is high, the recovered oxide is often white. For accurate work we recommend purification in *all* cases: the oxide is fused with a little sodium hydroxide in a nickel crucible, and the mass is dissolved in half-saturated sodium chloride solution.[10] The liquid is filtered through a small compact pad of filter-pulp; washing is carried out with half-saturated sodium chloride solution. The filtrate is treated with hydrochloric acid, tannin and cinchonine, etc., as before. This treatment yields pure tungstic oxide.

E. Results of Test Analyses.—The 14 analyses given in the next Table were carried out by the above procedure, except that in Exps. 9 and 10 we tried

	Taken				Found			
Exp.	M_2O_5 g.	WO_3 g.	Other oxides g.		*HP* g.	WO_3 in *HP* g.	WO_3 Error g.	Minor WO_3 fraction g.
9*	Ta_2O_5 0·2058	0·0164	—		0·2197	0·0159	−0.0005	(*n*)
10*	Nb_2O_5 0·2032	0·0180	—		0·1626	0·0128	−0.0052	(*n*)
11*	Ta_2O_5 0·2052	0·0145	—		0·2191	0·0142	−0.0003	Not detected (*a*)
12*	Ta_2O_5 0·1532 Nb_2O_5 0·0519	0·0158	—		0·2201	0·0154	−0.0004	0·0004 (*b*)
13*	Ta_2O_5 0·1084 Nb_2O_5 0·1073	0·0160	—		0·2278	0·0148	−0·0012	0·0004 (*b*)
14*	Ta_2O_5 0·0567 Nb_2O_5 0·1534	0·0140	—		0·2174	0·0132	−0·0008	0·0008 (*b*)
15*	Nb_2O_5 0·2056	0·0151	—		0·2120	0·0128	−0·0023	0·0007 (*a*)
16*	Ta_2O_5 0·1044 Nb_2O_5 0·1073	0·0170	TiO_2	0·0546	0·2351	0·0157	−0·0013	(*n*)
17*	Ta_2O_5 0·1064 Nb_2O_5 0·1020	0·0153	ZrO_2	0·0531	0·2377	0·0145	−0·0008	(*n*)
18*	Ta_2O_5 0·1056 Nb_2O_5 0·1020	0·0170	ThO_2	0·0544	0·2306	0·0162	−0·0008	0·0012 (*b*)
19*	Ta_2O_5 0·1061 Nb_2O_5 0·1030	0·0192	U_3O_8	0·0555	0·2029	0·0172	−0·0020	(*n*)
20*	Nb_2O_5 0·1034	0·0184	TiO_2	0·1017	0·1308	0·0165	−0·0019	(*n*)
21*	Ta_2O_5 0·2031	0·0034	—		0·2069	0·0031	−0·0003	(*n*)
22*	Nb_2O_5 0·2032	0·0027	—		0·1975	0·0026	−0·0001	(*n*)

* Quantities taken not known to operator. (*a*) By ammonia precipitation (see B); collector Fe_2O_3. (*b*) By double tartaric hydrolysis (see C). (*n*) Not recovered.

the effect of a higher concentration of hydrochloric acid (50 instead of 25 ml.); this gave a poor recovery of niobium and, consequently, of tungsten (Exp. 10), and was therefore abandoned. The other 12 tests comprise 10 on about 0·015 g., and 2 on 0·003 g., of tungstic oxide (Exps. 21, 22). Of the 10 mixtures with high tungsten-content, five (Exps. 11 to 15) form a graded series in which the niobic oxide content of the pentoxides rises from 0 to 100 per cent.; the remaining 5 tests (Exps. 16 to 20) illustrate the effect of titanium,[11] zirconium,[11] thorium,[12] and uranium,[13] which have been shown to affect the precipitation of the earth acids by tartaric hydrolysis. Exp. 20 demonstrates the probable course of the reaction with a titanoniobate mineral free from tantalum.

The minor tungsten fraction was recovered in 6 tests (last column of Table). We consider double tartaric hydrolysis (C, *supra*) to be relatively the best method, both precipitations being carried out on a bulk of 150 ml. with 25 ml. of hydrochloric acid. The tungstic oxide was determined in the small tannin-cinchonine precipitate of the minor fraction by Tschernichow and Karsajewskaja's colorimetric method.[14] Proceeding in this manner, we secured a complete recovery in 3 tests (Exps. 12, 14, 18), the last of which gave a positive error. However, we feel confident that the tungsten-content of earth-acid minerals can be satisfactorily ascertained without recourse to the tedious double treatment. The following considerations are intended to make this clear.

Most of the published analyses of earth-acid minerals in which the presence of tungsten is reported show a low tungstic oxide content (of the order of 0·5 per cent.). That this amount can be determined with a very small negative error by our procedure in 0·5 g. of mineral is proved by Exps. 21 and 22; hence we have only to discuss the fate of larger quantities of tungsten, as used in Exps. 11 to 20. Judged by their relative accuracy, these tests fall into 3 groups:

(i)	Error, 0·0003 to 0·0004 g.:	Exps. 11, 12
(ii)	,, 0·0008 ,, 0·0013 g.:	,, 13, 14, 16, 17, 18
(iii)	,, 0·0019 ,, 0·0023 g.:	,, 15, 19, 20

In Group (i) a good tungsten recovery is achieved, evidently due to the high tantalum-content of the oxide mixture. Group (ii) comprises mixtures of lower tantalum-content, with and without titania, zirconia or thoria; titania seemingly induces a slightly lower tungsten recovery (Exp. 16). In Group (iii) the effect of the absence of tantalum closely links Exps. 15 and 20; these, it should be remarked, represent unlikely cases in mineral analysis, as no high tungsten-contents have so far been reported in niobate and titanoniobate minerals. There remains Exp. 19, in which the shortage in weight of *HP*, caused by uranium, gave us the opportunity to predict a high tungsten-recovery error. As uranium is a frequent, though usually minor, constituent of earth-acid minerals, its interference in the tungsten recovery by tartaric hydrolysis is of particular interest to the mineralogist.

F. Determination of Correction Factor.—We have refrained from further tests because the number of qualitative and quantitative variables presented by earth-acid minerals is too great for an exhaustive investigation by means of synthetic oxide mixtures. In our opinion, the data required for the computation of a correction factor can only be obtained by numerous mineral analyses by the tartaric acid method. When an analysis has been concluded, a synthetic oxide

mixture should be subjected to the same process under identical conditions, the negative error in the tungsten recovery being added to the value obtained in the analysis of the mineral. This mixture should be made up of exactly the same quantities of the oxides of tantalum, niobium, uranium, titanium, zirconium and thorium as those obtained, *plus* a little (0·0003 to 0·002 g.) more tungstic oxide than that found by analysis. This excess is estimated by comparison of the mineral constituents with our synthetic oxide mixtures. If the operator has no pure oxides at his disposal, recourse may be had to the products of his analysis. Directions for carrying out the analysis will be found in Section 27[8] and under B above, it being understood that the volume of the liquid from which the metallic acids are precipitated by tartaric hydrolysis is 150 ml. It should be mentioned that our tungsten determinations by the magnesia method in Exps. 9 to 22 were done by a single treatment, our earlier tests having shown that the double treatment recommended in Section 29[15] produced no appreciable increase in the tungsten recovery from less than 0·25 g. of hydrolysis precipitate.

As a result of this research we have to revise the conclusion reached in Section 26, and quoted in our preamble, as to the position of tungsten in the tartaric-acid method of analysis. The element definitely belongs only to the group of the metallic acids precipitated by tartaric hydrolysis; in the subsequent determination of the other earths the elusive minor tungsten fraction may be safely neglected. On the strength of our experience, we believe that the tungsten-contents reported in the published analyses are slightly low.

G. Detection of Tungsten.—In the course of our work we had ample opportunity to observe that the detection of small quantities of tungsten is unsatisfactory. The stannous chloride test is neither rapid nor very sensitive. We investigated Defacqz's test,[16] consisting in the addition of solid phenol or hydroquinone to the cold solution obtained by fusing the oxide with a little bisulphate and adding enough strong sulphuric acid to prevent solidification on cooling. Tungsten gives intense colours (reddish-brown and violet with phenol and hydroquinone, respectively). But apart from the known fact that titanium reacts just as strongly, we found that niobium (the element which follows tungsten most tenaciously) also gives vivid colour reactions (orange-yellow and deep reddish-brown), whilst tantalum and zirconium do not react. As Defacqz's test is not specific, it cannot be applied to mixed oxides.

We tested the sensitiveness of the cinchonine reaction under the conditions of Exps. 3 to 8: tungstic oxide was fused with bisulphate (4 g.), and the solution (300 ml.) treated with ammonium chloride and ammonia. It was then acidified with hydrochloric acid, treated with cinchonine reagent, and concentrated by boiling. The liquor remained perfectly clear until concentrated to about 50 ml., when it began to opalesce. Evaporation was continued to the point of crystallisation. The salts were dissolved in water, and the flocculent precipitate collected, ignited, and weighed. In Exp. 23, 0·0028 g. of tungstic oxide thus gave a recovery of 0·0021 g. This proves that too much reliance should not be placed on the sensitiveness of the cinchonine test under the conditions described.

Summary.—The small amounts of tungsten frequently present in earth-acid minerals are precipitated with the earth acids by tartaric hydrolysis at fairly high

concentration under standardised conditions, and are determined in the hydrolysis precipitate by the magnesia method. If the tungstic oxide content of the mineral is high (the recorded maximum being about 3 per cent.), its determination by the proposed method involves a negative error increasing from about 0·0003 g. (with minerals high in tantalum) to about 0·002 g. (with minerals high in niobium or uranium). For high tungsten-contents we recommend a correction factor, to be determined by experiment on a synthetic oxide mixture or on the earths recovered in the analysis. The inadequacy of certain qualitative tests for tungsten is briefly noticed.

References

1. W. R. Schoeller and C. Jahn, ANALYST, 1934, **59**, 465.
2. A. R. Powell, W. R. Schoeller and C. Jahn, *id.*, 1935, **60**, 506.
3. W. R. Schoeller and H. W. Webb, *id.*, 1934, **59**, 670.
4. —— *id.*, 1936, **61**, 237.
5. W. R. Schoeller, *id.*, 1931, **56**, 305.
6. W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 1929, 551, footnote 7.
7. *Cf.* W. R. Schoeller and H. W. Webb, ANALYST, 1934, **59**, 668.
8. —— *id.*, 669.
9. W. R. Schoeller, *id.*, 1931, **56**, 308.
10. W. R. Schoeller and C. Jahn, *id.*, 1927, **52**, 513.
11. W. R. Schoeller and H. W. Webb, *id.*, 1929, **54**, 706.
12. W. R. Schoeller and E. F. Waterhouse, *id.*, 1935, **60**, 289.
13. W. R. Schoeller and H. W. Webb, *id.*, 1933, **58**, 147.
14. J. A. Tschernichow and M. P. Karsajewskaja, *Z. anal. Chem.*, 1934, **98**, 106; Abst., ANALYST, 1934, **59**, 717.
15. A. R. Powell, W. R. Schoeller and C. Jahn, *id.*, 1935, **60**, 513.
16. E. Defacqz, *Compt. rend.*, 1896, **123**, 308.

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The Standardisation of Hortvet Thermometers

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THE thermometers issued with the Hortvet apparatus are of mercury in glass, graduated from +1·0° C. to −2·0° C., the length of one degree being about 10 cm. The method of standardisation adopted by Hortvet was as follows:—two thermometers were standardised as carefully as possible at the American Bureau of Standards and using these thermometers with Hortvet's apparatus and procedure the freezing-point depressions were obtained of solutions made by dissolving 7 and 10 g. of sucrose in water and making up each solution to 100 ml. at 20° C. The pure sucrose was obtained from the Bureau of Standards. It has been ascertained that these two thermometers would be standardised to an accuracy of ±0·002° C. to ±0·005° C., although the corrections would be stated to 0·001° C.

Under the conditions of working, the differences between the freezing-points of water and of the solutions were found to be 0·422° C. and 0·622° C. for the 7 and 10 per cent. w/v solutions, respectively, for one thermometer, and 0·422° C. and 0·621° C. for the other; the interval 0·199° C. was accepted as the interval between the freezing-point depressions of 7 and 10 per cent. w/v sugar solutions.

Exactly the same procedure was followed for other thermometers and, if necessary, a factor was applied to the readings to convert the differences between the freezing-point depressions of the two sugar solutions to 0·199° C. This factor was then applied to all readings of freezing-point depression obtained by using the same thermometer, apparatus and procedure.

The A.O.A.C. suggest the standardisation of Hortvet thermometers at two definite points, *viz.* —0·422° C. and —0·621° C. As neither of these two temperatures is one which is met with in the examination of genuine milk, it is necessary to standardise at intermediate temperatures. The A.O.A.C. suggest that this be done in the following manner:

The thermometer is checked against each of the sucrose solutions. The freezing-point depression of each of these two solutions is taken in turn, using the thermometer to be tested. The interval between the two readings obtained is compared with the standard interval of 0·199° C. Thus in the case of a thermometer, in which the interval found was 0·205° C. (readings of —0·420° C. and —0·625° C., respectively), the correction for a reading of 0·548° C. would be obtained by the expression (0·548° C. — 0·420° C.) 0·971* = 0·124° C., and, corrected, the depression would therefore be 0·422° C. + 0·124° C. = 0·546° C.

This method of examination assumes that any error in a thermometer between the two points corresponding with —0·422° C. and —0·621° C. will increase or decrease uniformly in proportion with the graduation marks of the thermometer from —0·422° C. to —0·621° C. This supposition is most unlikely to be true, as it depends on equidistant spacing of the graduations, and also on the uniformity of the bore of the capillary tube between these two points. Errors may arise from either or both of these causes, and it is necessary to fix more definitely some of the intermediate points. As a first approximation[1] we suggested the freezing-point depressions of sugar solutions of intermediate strengths between the 7 per cent. w/v and 10 per cent. w/v solution of the A.O.A.C., the freezing-point depressions of these being found by interpolation by simple proportion.

As the Hortvet sugar solutions are made up by weight in volume of solution and not by weight in weight of solvent, the freezing-point depressions of solutions of intermediate strengths will not be exactly proportional to the quantity of sugar dissolved, but the error involved will not be large, as the standard is fixed at both ends of the scale. Whilst, for the purposes of the ordinary examination of milk, an error in the thermometer of the order of ±0·002° C. is of no vital importance, we felt the necessity, for the purpose of carrying out work on the more theoretical questions of cryoscopy, of being able to fix the intermediate points more closely than this.

In order to calculate the freezing-point depressions of sugar solutions of intermediate strengths between 7·0 per cent. w/v and 10 per cent. w/v (every 0·5 per cent. w/v) by means of Raoult's formula, it is necessary to know the amount of sugar dissolved in 100 g. of water in each case. We have carefully determined this figure, on the seven sucrose solutions concerned, by weighing out the necessary

* Interval on thermometer under test = 0·205, standard interval 0·199; therefore the factor becomes $\frac{0·199}{0·205} = 0·971$.

amount of sugar, transferring it to a clean and tared 200-ml. graduated and calibrated flask, dissolving the sugar in water, and making up to the mark after the flask had been allowed to stand in a thermostat at 20° C. ± 0·1° C. for one hour. The flask and contents were weighed, and the weight of sugar dissolved in 100 g. of water, was calculated in each case. The following results were obtained:

TABLE I

"TRUE" FREEZING-POINT DEPRESSIONS OF RAOULT'S SUCROSE SOLUTIONS

Grams of sucrose in 200 ml. of solution	Grams of water in 200 ml. of solution	Grams of sucrose in 100 g. of water	Δ °C. (calc. from Raoult's formula)
14·0	190·83	7·336	0·4103
15·0	190·22	7·886	0·4417
16·0	189·60	8·439	0·4735
17·0	188·97	8·996	0·5056
18·0	188·35	9·556	0·5379
19·0	187·75	10·120	0·5706
20·0	187·15	10·687	0·6037

A similar determination has been made by Monier-Williams[2] for the 7 per cent. w/v and 10 per cent. w/v solutions, results of 7·3373 and 10·6895 being obtained. These two different determinations are in close agreement, the difference only just affecting the fourth place of decimals in the freezing-point depression.

The 7·336 per cent. w/w solution (7·0 per cent. w/v Hortvet) was found experimentally by Hortvet to have a freezing-point depression, in his cryoscope and by his technique, of 0·422° C., and this figure has been adopted by the A.O.A.C. as one of the standards with which all similar thermometers are to be compared. For the 10·687 per cent. w/w solution (10·0 per cent. w/v Hortvet) the corresponding figure is 0·621° C. When the freezing-point depressions of these two solutions are calculated by means of Raoult's formula,

$$\text{F.P.D.} = \frac{18{\cdot}72 \times \text{P}}{342 - (0{\cdot}99 \times \text{P})}$$

where P = the concentration of the sucrose solution expressed in grams of sucrose per 100 g. of water, the figures obtained are 0·4103° C. and 0·6037° C., respectively. There is thus a difference between the Hortvet figure and the Raoult figure of 0·0117° C. at −0·41° C. and 0·0173° C. at −0·60° C.

These differences are, of course, caused by the fact that the Raoult figures are "corrected," whilst the Hortvet figures are "uncorrected." (For a detailed consideration of these points see J. R. Stubbs.[3])

There is at least good reason to suppose that the difference between the two readings (Hortvet's and Raoult's) will be more or less proportional to the depressions, so that, at least as a first approximation, if we assume 0·0117° C. as the difference at 0·41° C., then the difference at 0·60° C. may be expected to be

$$\frac{0{\cdot}0117° \text{ C.} \times 0{\cdot}6037}{0{\cdot}4103} = 0{\cdot}0172° \text{ C.}$$

The actual difference is 0·0173° C., so that the agreement is extremely close and is

valuable evidence of the mutual concordance of the two results obtained by Hortvet as his reference temperatures.

Having fixed the two extremes, it is possible to calculate the Hortvet freezing-point depressions of the intermediate solutions. The results obtained are shown in the following table:

TABLE II

FREEZING-POINT DEPRESSIONS (HORTVET) OF SUCROSE SOLUTIONS

Strength of sucrose solutions		Freezing-point depression (Raoult) °C.	Calc. Hortvet		Suggested Hortvet standard freezing-point depression °C.
Grams per 100 ml. of solution	Grams per 100 g. of water		Correction to be added °C.	Total °C.	
7·0	7·336	0·4103	0·0117	0·4220	0·422
7·5	7·886	0·4417	0·0126	0·4543	0·454
8·0	8·439	0·4735	0·0135	0·4870	0·487
8·5	8·996	0·5056	0·0144	0·5200	0·520
9·0	9·556	0·5379	0·0153	0·5532	0·553
9·5	10·120	0·5706	0·0163	0·5869	0·587
10·0	10·687	0·6037	0·0173	0·6210	0·621

It will be observed that very little correction is necessary to round off the figures to three places of decimals. In order, therefore, that the method of standardisation should be as uniform as possible, the figures given in the last column are suggested as standard Hortvet reference points at the intermediate temperatures. If, for any purpose, further intermediate temperatures are required, solutions of suitable strength may be prepared and their freezing-point depressions calculated by simple proportion, from any two adjacent pairs of figures, as any error involved is negligible.

REFERENCES

1. G. D. Elsdon and J. R. Stubbs, ANALYST, 1934, **59**, 589.
2. G. W. Monier-Williams, ANALYST, 1933, **58**, 258.
3. J. R. Stubbs, *id.*, 1935, **60**, 147, 223.

GENERAL REFERENCES

Lord Kelvin (Sir Wm. Thomson), *Math. & Phys. Papers*, 1848, Vol. I, p. 100.
P. Chappuis, *Travaux et Mémoires du Bureau international des Poids et Mesures*, 1888, Vol. VI.
C. R. Robertson and V. K. La Mer, *J. Phys. Chem.*, 1931, **35**, 1953.
H. L. Callendar, *Phil. Mag.*, 1903, **5**, 48.
H. L. Callendar and E. H. Griffiths, *Phil. Trans.*, 1891, [A], **182**, 119.
Ch.-Ed. Guillaume, *Traité practique de Thermométrie de précision*, 1889.
P. Chappuis, *London, Edinburgh & Dublin Phil. Mag.*, 1900, [5th Series], **50**, 453.
E. Buckingham, *Bulletin of the Bureau of Standards*, 1912, Vol. VIII, No. 2.
—— *Sci. Papers of the Bureau of Standards*, No. 57.
G. K. Burgess, *Bureau of Standards Research Paper*, No. 22.
C. W. Waidner and H. C. Dickinson, *Bulletin of the Bureau of Standards*, Vol. III, No. 4.
W. F. Higgins, *Dictionary of Applied Physics*, 1922, Vol. I, 988.
A. L. Day and R. B. Sosman, *id.*, p. 837.
E. Griffiths, *Methods of Measuring Temperatures*, London, 1925.
Bureau of Standards, Circular No. 8, 1926.
Ch.-Ed. Guillaume, *La Création du Bureau international des Poids et Mesures*, 1927.
Report of the National Physical Laboratory, 1928, p. 29.

LANCASHIRE COUNTY COUNCIL LABORATORY
LIVERPOOL

Anaesthetic Ether: The Effect of Some Impurities. Peroxides

By J. H. COSTE, F.I.C., F.Inst.P., and D. C. GARRATT, B.Sc., Ph.D., F.I.C.

(*Read at the Meeting, May* 6, 1936)

The necessity for the production of a very pure ether to be used in anaesthesia has been emphasised repeatedly in the literature, especially with regard to the absence of even extremely small amounts of peroxides. Undoubtedly autoxidation of ether is closely related to its initial purity, ether which is initially free from decomposition products showing little tendency to oxidise, and we find it difficult to obtain a high concentration of oxidation products from a pure ether, even after some months. Clover[1] found no better method of oxidation than exposure to light, formation of peroxide proceeding at a gradually increasing rate, especially noticeable during summer. The peroxidation has been shown to be due to acetaldehyde and, as this is also a decomposition product of the pre-formed peroxide, the rate of oxidation progressively increases. For our preliminary experiments difficulty was experienced in obtaining naturally highly peroxided ethers which we felt were necessary for significant results, and we confirm the findings of Middleton and Hymas[2] that samples of purified ether vary considerably in susceptibility to oxidation. The fairly recent work by King[3] on the cause of autoxidation suggests the probability of the peroxides present in ether being a mixture of a monacetaldehyde hydrogen peroxide and hydrogen peroxide, although there are indications of the presence of a further, more stable peroxide. Important for this paper is his observation that the peroxide could be almost quantitatively separated by distillation in an 8-bulb pear fractionating column. Lately, Bonz[4] has asserted that the photochemical formation of peroxide is independent of atmospheric oxygen. Middleton and Hymas[5] have studied the effects of certain gases on the oxidation of ether; they used conditions which were much more stringent than those of medical practice and would favour peroxide formation, but, as the following experiments will show, would be less likely to affect the ether which the patient would receive. The peroxide in samples of fairly pure ether was increased somewhat, but when the effluent gas was bubbled through water in no case was peroxide detected.

Little systematic work has been conducted on the question of preventing autoxidation of ether, although as accumulation of peroxide is due to deterioration, initial purity is better than the use of a stabiliser. Many reducing agents added in small quantities have been proposed (Nolan,[6] Palkin and Watkins[7]); Hewer[8] suggested that the rate of decomposition of ether would be greatly diminished if there were an adequate area of copper above and below the ether level.

When ether is used for anaesthesia, the primary consideration is necessarily the patient, and it has been widely assumed that, to prevent undesirable after-effects, the ether used must be free from oxidation products, such as acetaldehyde and peroxides (which are believed to be toxic). Dale and King,[9] however, in 1925 (Hadfield,[10] a retrospect of 11 years' work of the Joint Anaesthetics Committee)

carried out a few experiments by administration of different samples of ether to cats, and these suggested that the bad effects of impure ether were due, not to the peroxides, but to some other undetermined substance. The presence of peroxides might be a fair index of the presence of such a substance. They were unable to continue their experiments further at the time, and up to the present have not published anything further on these lines.

At a discussion on late ether convulsions, Hadfield[11] pointed out that peroxides, owing to their low volatility, should not pass over to the patient, but accumulate in the apparatus used when fresh ether is added. He was of the opinion that peroxides were not the cause of the symptoms. In the discussion, opinion differed as to whether impurities in the ether were possibly of less importance than other factors. A peculiar unexplained feature is the absence of any record of such cases prior to 1926. It is still uncertain whether the presence of peroxides is indicative of an ether which will produce symptoms of late ether convulsions, and the cause of this somewhat rare complication during ether anaesthesia must not be confused with the question of unpleasant after-effects produced by use of deteriorated ether.

At the request of the Medical Officer of Health, the question of the decomposition of ether is being systematically re-investigated by us, and, after preliminary experiments which are not of import here, confirmation of results of previous workers was obtained, the practical application of these conclusions appearing to be that ether used for anaesthetic purposes should be stored in the dark, that only small bottles filled almost to the stopper should be used, and that these should be wrapped in black paper not reaching all round, leaving a vertical slit through which the level of the ether can be observed.

Consideration of the probability that ether peroxide was less volatile than ether itself, a probability supported by the observation of King (*loc. cit.*[3]) that the peroxide could be separated almost quantitatively from ether by fractional distillation, led the investigation into a new channel. The experimentation adopted was based rather on the degree of contamination of the vapours which the patient receives under anaesthesia than on the quality of the ether used, and all work is being concentrated on the products of volatilisation. The first point to be cleared up was that of contamination by peroxide, and this note is the result of our experiments on this question.

The apparatus used for preliminary experiments was designed to obtain a long contact between the ether and the gas and afterwards efficient condensation of the vapour phase; the former object was attained by use of a Winkler absorption tube (about one metre long) in which air was bubbled through the ether, and the latter by condensation of whatever was evaporated by this means in White's absorption tubes immersed in alcohol and solid carbon dioxide (— 75° C.). The apparatus was all glass, and is best described by diagram (see Fig. 1).

To determine the relative amounts of peroxide, the ferrous thiocyanate method, as described by Middleton and Hymas (*loc. cit.*[2]), was used. We have found the test to be the most sensitive of those that have been described. It has also the advantage of being most suitable for quantitative work as the "intensity of colour is most nearly proportional to the amount of peroxide present, and it can be observed over a sufficiently wide range." Dilutions were made so that the colour

matched was not more than about 6 red units in a 1-cm. cell on the Lovibond tintometer (B.D.H.), allowance being made in calculation for a trace of peroxide in the ether used for dilution. All red values recorded are calculated on the original volume of ether taken for the particular experiment, and if necessary can be easily correlated with parts per million (*cf.* Middleton and Hymas). An ether which was considered just not to pass the B.P. limit test for peroxides had a red value of 2·4.

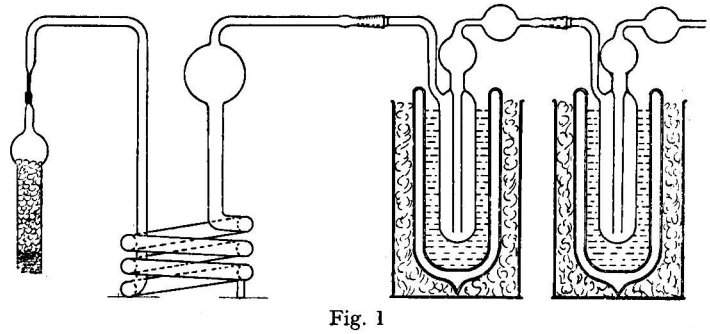

Fig. 1

Table I summarises the experiments first carried out, and, in view of the statements prevalent in the literature on the subject, they were begun with cautious evaporation of the ether by a current of dry air in the dark to prevent or retard formation of peroxide. Later, from observations during the course of experimentation, screening of the apparatus and drying of the air were abandoned, and conditions assumed to be productive of decomposition were invited. It will be seen that no appreciable increase in peroxide was found under the conditions used, and that peroxide was not volatilised in appreciable amount.

TABLE I

VOLATILISATION OF ETHER BY BUBBLING AIR THROUGH IT

	Ether used				Residue		Condensate			Observations under conditions of experiment
	ml.	Red value	Air litres	Time Hours	ml.	Red value	ml	Red value	Loss ml.	
1	59	1·2	5	3·0	36·0	0·7	22·5	0·3	0·5	No increase in peroxide. No appreciable volatilisation of peroxide.
2	61·5	69·6	5	3·0	37·0	68·9	23·0	0·8	1·5	
3	58·5	389	2·7	2·0			10·0	0·7		Peroxide does not volatilise until practically all ether removed. No appreciable volatilisation of peroxide with increased rate of bubbling.
			2·7	1·5			11·5	0·6		
			2·4	2·0			9·4	0·4		
			2·4	1·5			13·0	0·4		
			2·5	1·0			10·0	0·3		
			1·6	0·7	1·0	428	1·0	6·0	2·6	
4	59	391	2	1·25			8·5	0·6		
			4	1·5			20·0	0·2		
			3	0·5			12·4	1·2		
			4	0·17	4·0	411	10·2	1·3	3·9	

In Exps. 1, 2 and 3, light and moisture were excluded and the temperature kept constant at 17·5° C.; in Exp. 4 bright sunlight and moist air were used, and

the vapour phase heated to 34 to 36° C. by exposing the first White's absorption tube to this temperature.

After these indications of the probability that peroxides themselves were of no consequence to the patient, since they could not normally reach him, conditions under which anaesthesia would be produced had to be simulated in the laboratory to correlate our findings with the more exacting conditions likely to be met with in practice. By the courtesy of Dr. Stebbings, of Lambeth Hospital, we were able to study these conditions during operations.

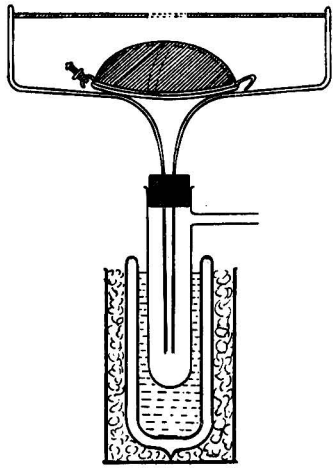

Fig. 2

For the "open mask" method of ether anaesthesia (see Table II), the modification shown in Fig. 2 of the apparatus previously used was designed.

At first, difficulty was experienced in obtaining good yields of condensate owing, amongst other things, to surging of the rapidly vaporised ether (Exps. 5 and 6), but this was improved by using a very large funnel and by covering the top of it with cardboard, a reasonably efficient recovery being obtained (Exps. 7 and 8).

In all the experiments the ether was poured from a dripping bottle over the entire surface of the muslin of the mask at such a rate as to keep the mask wetted. Immediately after the ether dripping was stopped, the mask was carefully removed (violent agitation of the vapour in the funnel being avoided), the muslin was at once put into pure ether in a covered beaker, macerated several times with further quantities of ether and finally wrung out, and the ether was made up to a definite volume.

The muslin of the mask was proved neither to catalyse production of peroxide nor to reduce the peroxide of the original ether. The muslin was steeped in highly peroxided ether for 15 minutes and washed out as described above; an ether with an original red value of 651 gave a recovered ether of red value 661 after this treatment.

TABLE II

VOLATILISATION OF ETHER FROM "OPEN MASK" APPARATUS

	Ether used				Residue on mask		Condensate		
	ml.	Red value	Time Minutes	Temp. °C.	ml.	Red value	ml.	Red value	Peroxide recovery Per cent.
5	39	391	8	23		184	7·0	2·0	47·6
6	40	178	10	23		128	2·0	0·7	72·3
7	39	276	15	22		226	15·4	1·7	83·7
8	37	276	15	19	8·0	270	4·6*	2·7	100·2
							13·6	2·0	
							2·0	1·8	

* Recovered in fractions.

No peroxide was found remaining in the mask-frame or funnel.

Experiments were then conducted with a Boyle's apparatus using nitrous oxide and oxygen in approximately equal proportions, bubbling the gases through or over the ether to produce a steady rate of vaporisation, the vapours being condensed in the White's absorption tubes as before. The experiments were conducted in sunlight at a temperature of about 22° C., and the ether in the bubbler was allowed to evaporate to only about half its volume. At first, the aqueous vapour from the bubbling gauge gave such a large condensation of ice in the White's tubes that they became blocked and ether escaped by back-pressure. This difficulty was mitigated to some extent by using nearly saturated calcium chloride solution at 0° C. in the gauge to reduce the aqueous vapour tension, and the mixed ether and gases were by-passed through the empty chloroform bottle which was immersed in ice. The condensation of aqueous vapour (red value very small) then did not prevent a free passage of gases; even so, the proportion of ether condensed in the White's tubes was small owing to the extremely rapid flow of vapours by the use of this apparatus. The red value of the condensate was so small, compared with that of the original ether, that it seems improbable that if all the liquid volatilised had been condensed it would have contained more than a very small proportion of the peroxide in the original liquid. The results are summarised in Table III.

TABLE III

VOLATILISATION OF ETHER FROM BOYLE'S APPARATUS

	Gases used	Ether vaporised		Time Minutes	Residue Red value	Condensate	
		ml.	Red value			ml.	Red value
9	O_2 and N_2O	61	1,326	30	1,576	4·5	10
10	O_2 and N_2O	50	1,611	40	1,526	10	20

The above experiments have been carried out with ethers so badly contaminated, that they could not possibly be used for anaesthetic purposes, and the proportion of peroxide volatilised and breathed by the patient is so small that for ethers only contaminated to the extent likely to be met with in general practice the actual peroxide volatilised would be negligible; also under conditions of anaesthesia the time is too short for the deterioration of the original ether to any great extent. Hence from the results obtained we must come to the conclusion that, although it is unquestionable that ether should be as pure as possible for anaesthesia, peroxides *themselves* are not the cause of the after-effects which may be produced by impure ether.

It is hoped that the study of other possible contaminants from the same angle may lead to results which will have a more constructive effect in eliminating undesirable after-effects from the use of ether.

REFERENCES

1. A. M. Clover, *J. Amer. Chem. Soc.*, 1922, **44**, 1107.
2. G. Middleton and F. C. Hymas, ANALYST, 1928, **53**, 201.
3. H. King, *J. Chem. Soc.*, 1929, 738.
4. C. Bonz, Abst., *J. Chem. Soc.*, 1933, A, 1385.
5. G. Middleton and F. C. Hymas, *Quart. J. Pharm.*, 1929, **2**, 278.

6. H. O. Nolan, *Lancet*, 1933, **225**, 129.
7. S. Palkin and H. R. Watkins, *Ind. Eng. Chem.*, 1929, **21**, 863.
8. C. L. Hewer, *Lancet*, 1929, **216**, 770.
9. H. H. Dale and H. King, *Lancet*, 1923, **204**, 425.
10. C. F. Hadfield, *Proc. Roy. Soc. Med.*, 1935, **28**, 1136.
11. —— *id.*, 1928, **21**, 1699.

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DISCUSSION

The PRESIDENT said that they should be very grateful for this paper, which, he thought, negatived the idea that these impurities were responsible for the unfortunate happenings which had occasionally occurred. Although he had always been sceptical about these impurities being the cause of these disasters, it was obvious that anaesthetic ether should be as pure as possible. It was only natural that an anaesthetist after such a fatality should raise these questions as part of a very natural desire to eliminate all possible factors. The London County Council had been very wise in requesting the authors to give this matter their consideration. He congratulated them on their paper.

Mr. G. MIDDLETON remarked that the results were very interesting, and indicated that no peroxide was carried over under the conditions of the experiments. But clinical evidence did point to irritation being set up by impurities present in ether; it might not be due to peroxide but to other impurities such as aldehyde, and he hoped that the authors would extend their investigations further. Unless it was very extensive, clinical evidence was always uncertain; it might be remembered that some fifteen years ago it was claimed that perfectly pure ether was not an anaesthetic—that had been disproved. If ether were initially quite pure and kept under reasonable conditions, it would not form peroxides, but sometimes the conditions of storage were not suitable. In the operating theatre ether might be left exposed to air and light, and could become badly contaminated. He remembered an experiment by Dr. H. O. Nolan, in which a heated glass rod was inserted momentarily into the mouth of a flask containing a little ether. A strong smell of ether peroxide was immediately observed, and the vapour gave a strong starch-iodide reaction. Did not the characteristic irritating smell of deteriorated ether indicate that ether peroxide was slightly volatile?

Mr. J. H. COSTE, replying, said that the views embodied in the President's remarks were those also formed by him (the speaker) and his colleagues at an early stage of their investigation. The matter had been referred to them by the London County Council Committee, and he thought that they had elucidated it to this extent—if, in administering ether, only the vapour was administered, the chances of peroxide being inhaled were very small. However old the ether might be, unless there were a cloud or fog, one would not administer peroxide. No apparatus used for giving ether was of the spray type, so that the patient received a mixture of air and "gas" vapour. But, of course, that was not to say that cases of injury which had been reported were not due to some impurities in the ether.

The Application of Diphenyl Thiocarbazone (Dithizone) to the Estimation of Lead in Urine

By F. MORTON, B.Sc., A.I.C.

It is generally accepted that, if sufficiently sensitive qualitative tests are applied, such as the triple nitrite method (Fairhall),[6] in which caesium nitrite is used at the final stage, many normal urines will give positive results for lead. Various values for the amounts of lead in normal urines have been recorded by different workers; Kehoe and Thamann,[11] from the analysis of urine of healthy students, found an average value of 0·08 mg. per litre; Rabinowitch, Dingwall and Mackay[15] give 0·1 mg. per litre as an average; Francis, Harvey and Buchan[9] found values ranging from nil to 0·133 mg. per litre, with an average of 0·04 mg. In an extensive series of investigations Kehoe, Thamann and Cholak (1933)[13] have shown that even certain primitive peoples living under conditions involving but the slightest intake of lead, excreted in their urine very small amounts of the metal traceable to a minute amount of lead in the native soil. These investigators found, generally, much larger amounts of lead in the excreta of people exposed industrially to the metal than in those of normal persons. The urinary differences between normal and lead-intoxicated persons are therefore determinable, and as an aid to diagnosis quantitative investigations of available material need to be carried out.

A review of the methods at present available for the estimation of lead in biological material indicates that few are acceptable for routine purposes in the clinical laboratory. Fairhall (1922)[5] described a chromate method for lead in urine, etc., which has been widely used in the original and modified forms during the last few years. Apart from the length of time required for the completion of these methods (4 to 8 days), there is some doubt whether lead can be quantitatively precipitated as chromate under Fairhall's conditions when less than 0·1 mg. of lead is present. Satisfactory recovery of added lead is reported by Myers, Gustafson and Throne,[14] who used a simple modification of Fairhall's method, but this has not been the experience in this laboratory. Kehoe *et al.*[12] in their investigations employed an elaborate chromate method, but a more recent publication by the same workers[13] discloses the occurrence of an approximately constant error of 0·07 mg. of lead per sample. This fact was only revealed when the chromate results were compared with those obtained by a spectrographic method (Cholak, 1935).[4]

Two electrolytic methods have been described in recent years. For lead in urine, Cooksey and Walton[3] (1929) have applied a process of direct electrolysis of the acidified sample, the metal deposited on the anode being dissolved and determined by a standard procedure. The method is simple and rapid, but no evidence is provided to justify the assumption that all the lead in urine is in the ionised form. A much more elaborate electrolytic method of wider application, requiring 3 to 4 days for completion, has been described by Francis, Harvey and Buchan.[9] Large amounts of reagents are required for the wet oxidation of the material;

this necessitates preliminary purification, and, together with the need of special expensive equipment, makes the method unsuitable for laboratories where only occasional demand arises for lead estimations.

A rapid method of lead estimation in urine, providing reasonably accurate results, seemed a need worthy of attention. The following aims have been kept in mind in developing such a method:—the volumes of reagents should be small to avoid the necessity for tedious processes of purification, there should be reasonable precision and specificity, and it should be possible to complete the estimation within approximately 24 hours of receiving the sample. A satisfactory procedure based on the separation of lead with diphenyl thiocarbazone has been worked out.

The studies of Fischer[7] and of Fischer and Leopoldi[8] have naturally led to the application of diphenyl thiocarbazone as an analytical reagent (Fischer,[7] Allport and Skrimshire,[1] Bohnenkamp and Linneweh,[2] 1933).

The technique of Allport and Skrimshire[1] was applied to the estimation of lead in urine, and proved unsatisfactory in certain respects. First, the process of wet oxidation of 500 ml. of urine involves the use of fairly large amounts of reagents, and is, moreover, a tedious task requiring considerable time and attention. Secondly, the strength of their dithizone solution, *viz.* 0·1 per cent. w/v, was much too great when only small amounts of lead were to be separated; the bright green colour of the excess of reagent completely masked the pink colour of the lead derivative. This rendered it impossible to decide whether or not the last traces of lead had been removed; and, furthermore, the presence of a large excess of free dithizone added to the difficulty of bringing to satisfactory completion the subsequent wet oxidation of the chloroform extracts. Lastly, the amount of cyanide used by Allport and Skrimshire in their extraction process was considered insufficient, since on several occasions violet extracts were obtained from which the colour was discharged by shaking with an additional quantity of cyanide.

METHOD: REAGENTS REQUIRED.

Dithizone Reagent.—A 0·05 per cent. solution of dithizone in chloroform is shaken with 10 per cent. ammonia in a separating funnel, the chloroform solution being afterwards extracted with fresh supplies of ammonia, until it no longer shows a green colour, whereupon it is discarded. The ammoniacal extracts are united and acidified with dilute sulphuric acid in the separating funnel, and the dithizone thereby precipitated is re-dissolved in pure chloroform to give an approximately 0·05 per cent. solution. This solution is diluted with equal volumes of pure chloroform as required for application in the analytical procedure. The stronger solution is stored in a dark coloured bottle not exposed to sunlight. Under these conditions it appears to keep well for 2 to 3 weeks.

Potassium cyanide, A.R.—1 and 10 per cent. solutions.

Ammonia, A.R.—2 and 10 per cent. solutions.

Ammonium citrate.—60 per cent. solution.

Hydrochloric acid, A.R.—10 per cent. and $N/10$ solutions.

The above aqueous solutions are made up with doubly distilled water.

ANALYTICAL PROCEDURE.—500 ml. of urine are treated with 10 ml. of strong ammonia solution and allowed to stand overnight. The phosphate precipitate

is filtered off on a No. 44 Whatman paper and Buchner funnel. The sides of the beaker are washed with a small amount of 2 per cent. ammonia, which is poured into the filter-funnel only when nearly all the urine has passed through. Gentle suction is applied to the filter until the precipitate is dry. The precipitate, together with the paper, is then ashed for 1 hour in a silica basin in a muffle regulated at about 500° C. The dish is allowed to cool, and the charred residue is treated with a few drops of conc. nitric acid, after which it is re-heated for half-an-hour. The ash, which should be almost white and free from carbon, is cooled and dissolved in 20 ml. of 10 per cent. hydrochloric acid, and the solution is boiled for a few minutes and filtered through a small paper. The dish and filter are washed 5 or 6 times with hot water. The filtrate and washings are cooled, and 10 ml. of 60 per cent. ammonium citrate solution, followed by 5 ml. of 10 per cent. potassium cyanide solution, are added. The liquid is then made just alkaline to litmus by the addition of 10 per cent. ammonia solution. A blank analysis of reagents is made at the same time.

The alkaline solution, which should be perfectly clear, is transferred to a 300-ml. separating funnel and vigorously shaken with 5 ml. of the dilute dithizone solution. In the presence of lead the chloroform is pink or violet, according to the amount of the metal present. The separated chloroform layer is removed, and the aqueous solution is shaken with another 5 ml. of dithizone solution. The process of lead extraction is continued in this way until the separated chloroform layer shows no suggestion of a pink colour after it has been washed with a solution containing 5 ml. of 1 per cent. potassium cyanide and 5 ml. of 2 per cent. ammonia mixed with 10 ml. of distilled water. This washing solution removes the greater part of the excess of free dithizone and renders it far easier to decide whether the lead has been extracted completely.

The combined chloroform extracts from the process still contain free dithizone, which must now be completely removed. The extract is placed in a small separating funnel and shaken with several fresh additions of the alkaline cyanide wash-solution mentioned above. Some means of preventing loss of extract during the washing processes has to be adopted, since chloroform is held in the surface of the aqueous layer. This can be done by mixing the wash-layers together, finally separating the accumulated chloroform at the end of the washing process and returning it to the main bulk of extract.

When the chloroform extract no longer contains free dithizone (as indicated by the clear and colourless appearance of the last cyanide wash-solution) it is washed with distilled water, and returned to the clean separating funnel. It is then shaken with 15 ml. of $N/10$ hydrochloric acid, whereby the pink lead dithizone derivative is decomposed into the equivalent amounts of free dithizone and lead chloride. The former dissolves in the chloroform layer, giving it a bright green colour, whilst the lead is taken up by the acid layer. The green chloroform solution is transferred to a 50-ml. volumetric flask, the acid layer being washed with re-distilled chloroform, and these washings added to the solution in the standard flask. After being made up to the mark with chloroform the solution is ready for colorimetric measurement. This can be effected either by direct comparison against a standard colour prepared simultaneously with the unknown from a standard solution

of lead, or by measurements of its extinction coefficient with the Zeiss-Pulfrich photometer as described below.

CALIBRATION OF THE ZEISS-PULFRICH PHOTOMETER.—The use of the Zeiss instrument eliminates the necessity of repeated preparation of standards for comparison, and also enables one to investigate the validity of Beer's Law for the colour to be measured. A series of standard lead solutions was prepared, and the lead extracted by the foregoing procedure. The chloroform extracts containing free dithizone were made up to 50 ml. and the extinction coefficients measured for each of the light-filters provided with the instrument. On plotting the extinction coefficients against mean wave-length of the series of light-filters, dithizone in chloroform was found to possess a maximum light absorption in the region of 610$m\mu$. This corresponds with the findings of Bohnenkamp and Linneweh,[2] who, in a more elaborate study of the absorption spectrum of dithizone in carbon tetrachloride, observed a maximum absorption at 630$m\mu$.

The light-filter corresponding with the region of maximum absorption was used in measurements of extinction coefficients in subsequent analyses. The dithizone extinction coefficients observed with this filter were plotted against the corresponding lead-contents of the standard lead solutions, and a curve indicating the direct proportionality existing between the lead and the dithizone with which it combines during the analytical procedure was obtained.

COLORIMETRIC COMPARISON.—If the Zeiss instrument is not available, a colorimeter can be applied either (i) by comparing the unknown with a standard prepared from a suitable lead solution extracted at the same time as the unknown solution, or (ii) by comparison with a solution of dithizone in chloroform containing 1 mg. per 100 ml. The second suggestion is based on measurements of the extinction coefficients of various concentrations of commercial dithizone dissolved in chloroform. The approximate absorption spectrum of such solutions corresponded with the curves previously obtained. It was also found that the colour of a solution of dithizone (1 mg. per 100 ml.) is equal in strength to that obtained from 0·09 mg. of lead when this is extracted by the above process, and the final volume of such extract is made up to 50 ml. volume.

Colorimetric comparison of weak solutions of dithizone must be made fairly rapidly, since a tendency to fading has been observed on several occasions. The standard prepared from the commercial chemical must be made up freshly as required.

METHOD OF CHECKING RESULTS BY A SULPHIDE PROCEDURE.—It is worthy of note that the foregoing procedure allows for a simple check on the analysis. After the lead dithizone extract has been shaken with acid at the final stage, the lead actually remains behind in the acid layer. In a few instances the acid layer has been analysed for its lead-content by a sulphide method. For this purpose the acid solution is washed 3 to 4 times with chloroform to remove completely all traces of dithizone, which would otherwise interfere with the subsequent sulphide comparison. The chloroform is removed, and the solution remaining heated on a boiling water-bath for several minutes. After cooling, the solution is made slightly alkaline with ammonia, and 1 gm. of ammonium acetate, followed

by 1 ml. of 10 per cent. sodium sulphide, is added. The solution is then compared with suitable lead standards in Nessler cylinders.

RESULTS OF ANALYSES.—The method of analysis described has been applied to a series of 24-hour specimens of urine collected from hospital patients who, for the most part, had no history of any industrial exposure to lead. A few of the patients in the series had been employed as plumbers and painters prior to their admission to hospital; they had been removed from abnormal exposure to lead, however, for periods ranging from 2 to 18 months, and showed no symptoms of lead poisoning. The urines from these patients showed no excess of any significance in lead-content compared with the others of the series (see Table I). This indicates that urinary lead examinations are useful in diagnosis only when the exposure to the metal

TABLE I

(*a*) *Urines from patients with no industrial connection with lead.*

17 analyses. Range nil to 0·11 mg. per litre.
nil to 0·12 mg. per 24 hours.
Average 0·04 mg. per litre.
0·05 mg. per 24 hours.

(*b*) *Urines from patients who had been removed for long periods from their occupational exposure to lead.*

8 analyses. Range nil to 0·14 mg. per litre.
nil to 0·11 mg. per 24 hours.
Average 0·05 mg. per litre.
0·05 mg. per 24 hours.

Of these 25 specimens, 23 contained less than 0·1 mg. of lead per litre, and 22 less than this amount per 24 hours.

TABLE II

RESULTS OF DUPLICATE EXPERIMENTS

Vol. of urine analysed ml.	Lead found mg.	Lead per litre mg.
500	0·02	0·04
700	0·03	0·045
800	Nil	Nil
800	Nil	Nil
500	0·04	0·08
350	0·03	0·085
700	0·01	0·015
700	0·015	0·02
500	Nil	Nil
500	0·01	0·02
375	0·025	0·065
375	0·025	0·065
550	0·04	0·075
750	0·06	0·08
400	0·025	0·06
400	0·025	0·06

TABLE III

RESULTS OF RECOVERY EXPERIMENTS

Vol. of urine ml.	Lead added mg.	Lead found mg.	Lead recovered mg.	Error
500	None	Nil	—	—
500	0·01	0·015	0·015	+0·005
500	0·03	0·035	0·035	+0·005
500	0·05	0·055	0·055	+0·005
600	None	0·03	—	—
600	0·05	0·08	0·05	0·00
500	None	0·04	—	—
500	0·08	0·10	0·06	−0·02
300	None	0·005	—	—
500	0·10	0·075	0·07	−0·03
500	None	0·01	—	—
500	0·10	0·08	0·07	−0·03
300	None	0·005	—	—
500	0·20	0·17	0·165	−0·035
400	None	0·03	—	—
400	0·20	0·20	0·17	−0·03
400	0·15	0·15	0·12	−0·03
400	0·10	0·11	0·08	−0·02
400	None	0·025	—	—
400	0·25	0·24	0·215	−0·035
500	None	0·025	—	—
500	0·10	0·11	0·085	−0·015
500	0·20	0·19	0·165	−0·035
500	0·40	0·36	0·335	−0·065
500	None	0·025	—	—
500	0·30	0·27	0·245	−0·055
400	None	0·025	—	—
400	0·20	0·19	0·165	−0·035
400	0·30	0·285	0·26	−0·04
500	None	0·02	—	—
500	0·05	0·07	0·05	0·00
500	0·15	0·15	0·13	−0·02
500	0·20	0·19	0·17	−0·03
600	None	0·035	—	—
600	0·10	0·110	0·075	−0·025
600	0·20	0·205	0·17	−0·03

All the results are to the nearest 0·005 mg.

has been recent. In this connection it is of interest to note the possible application of lead-excretion measurements, following low calcium with high phosphorus diets, as an aid to diagnosis of lead intoxication (Gray).[10]

A number of analyses have been duplicated, and the results, shown in Table II, indicate the consistency attainable.

The results of a number of recovery experiments are given in Table III. In these experiments known amounts of lead were added as lead acetate to the urines prior to precipitation of the phosphates.

Examination of the recorded recovery experiments discloses that there is a loss of lead during the process, except when the amount of lead added is small. It also appears that the magnitude of the error increases as the amount of lead to be removed increases. It is very probable that incomplete precipitation of lead with phosphate at the first stage of the procedure, and some loss of lead by volatilisation during ashing, are the chief factors responsible for these errors. Loss of lead due to its incomplete precipitation with the phosphate has been recorded in the literature, and Fairhall has stated that this can be minimised by the use of fresh urine for the analysis.

Where urine analyses for lead are to be carried out as part of precise studies of metabolism it would appear advisable to replace phosphate precipitation by a process of wet oxidation. For routine purposes, however, it usually would be sufficient to employ the less tedious of the two procedures.

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REFERENCES

1. N. L. Allport and G. H. Skrimshire, ANALYST, 1932, **57**, 440.
2. H. Bohnenkamp and W. Linneweh, *Arch. Klin. Med.*, 1933, **175**, 157.
3. T. Cooksey and S. G. Walton, ANALYST, 1929, **54**, 97.
4. J. Cholak, *J. Amer. Chem. Soc.*, 1935, **57**, 104.
5. L. T. Fairhall, *J. Ind. Hyg.*, 1922, **4**, 9.
6. —— *J. Biol. Chem.*, 1923, **57**, 455.
7. H. Fischer, *Z. angew. Chem.*, 1929, **42**, 1025; *Mikrochem.*, 1930, **8**, 319.
8. H. Fischer and G. Leopoldi, *Z. angew, Chem.*, 1934, **47**, 90.
9. A. G. Francis, C. O. Harvey and J. L. Buchan, ANALYST, 1929, **54**, 725.
10. I. Gray, *J. Amer. Med. Ass.*, 1935, **104**, 200.
11. R. A. Kehoe and F. Thamann, *id.*, 1929, **92**, 1418.
12. R. A. Kehoe, F. Thamann and J. Cholak, *J. Ind. Hyg.*, 1933, **15**, 257.
13. —— *J. Amer. Med. Ass.*, 1935, **104**, 90.
14. C. N. Myers, F. Gustafson and B. Throne, *J. Lab. Clin. Med.*, 1935, **20**, 648.
15. I. M. Rabinowitch, A. Dingwall and F. H. Mackay, *J. Biol. Chem.*, 1933, **103**, 725.

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 CARBON DIOXIDE IN BIOLOGICAL FLUIDS, MORE PARTICULARLY MILK AND CREAM

A SIMPLE method for determining carbon dioxide in carbonates, by absorption in standard baryta of the gas liberated at low pressure, has been described by Hepburn (ANALYST, 1926, **51**, 622). The application of the method to biological liquids has hitherto been limited by the frothing of the liquid. This difficulty can be overcome, however, by addition of a protein precipitant to the acid used for setting free the carbon dioxide from the biological fluid. The method has been applied with success to milk and cream.

The protein precipitant used may be phosphotungstic acid, silicotungstic acid, or phosphomolybdic acid (10 parts) dissolved in 100 parts of 5 per cent. sulphuric acid.

The apparatus has been designed to eliminate the necessity for disconnecting it between successive determinations (see Fig. 1). The flask B is of the smallest size that will give the necessary free space for ebullition with the quantity of liquid under examination (for milk and cream I have used 800-ml. and 1000-ml. flasks); C and D are graduated separating funnels. The tubulure L is joined to the bulb of the flask in such a direction that, when the apparatus is in its final position, the inner tube will reach to the lowest portion of the bulb; the other two tubulures are so bent as to be vertical when the flask is in its final position. G is a flat-bottomed flask, of a size to correspond with the flask B. It should not be too small, since space must be provided for the displacement of some residual air from B (I have used 100-ml. and 200-ml. flasks for milk and cream). F is a screw clip; I and H are glass taps. J is a rubber stopper of a size to fit flasks G. In the event of the quantity of baryta solution in G being inadequate for the amount of carbon dioxide evolved, as indicated by the disappearance of the phenolphthalein colour, a second flask containing baryta can be attached at J, and, after evacuation, can be connected by means of tap H, K being closed with a screw-clip. A is a large Buchner flask connected to a water-pump. The system is connected to a manometer and Hyvac pump at K.

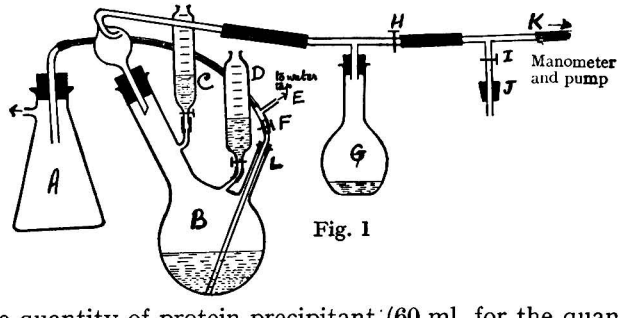

Fig. 1

The requisite quantity of protein precipitant (60 ml. for the quantities of milk and cream specified below) is run into B from C, and the required measured volume of standard baryta ($N/10$) is placed in G. The whole system is evacuated, the acid solution is heated to boiling for a few seconds to drive off air and any dissolved carbon dioxide, and the tap H is closed. The requisite volume of liquid to be examined (100 ml. of fresh milk or cream; 50 ml. of stale milk or cream) is run in

from D, and the contents of B are heated with a naked flame, flask G being alternately shaken, and cooled by immersion in a dish of cold water. Any tendency of the liquid in B to froth over can easily be corrected by a momentary concentration of the heating on the open side of B (the left-hand side in the figure). Absorption is complete in 2 to 4 minutes, when the barium carbonate precipitate in G will be seen to settle out, leaving a clear watery surface on the residual baryta. Taps I and H are then opened, and G is disconnected for titration with $N/10$ oxalic acid. With the water-pump running, the screw clip F is opened, and the contents of B are drawn out into A. If rinsing of B is required, the rubber tube above the outlet E is pinched with the fingers, and the water tap is turned on. The washings are drawn out into the reservoir A, and the apparatus can then be used for another determination.

Freshly-boiled milk has been found to give a good blank, and added carbonate can be accurately determined in milk or cream. The method could readily be adapted for the determination of carbon dioxide in liquids other than milk or cream (*e.g.* beer), and could easily be modified for use on the semi-micro- or micro-scale.

F. H. McDOWALL

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THE CHLORINE-CONTENT OF FEATHERS

IN the paper read before the North of England Section on February 1st, 1936, by Mr. F. Robertson Dodd (ANALYST, 1936, 252), it would seem that he had overlooked data previously published in THE ANALYST (1928, **53**, 278). In that contribution are given a dozen or more determinations of oxygen absorbed and chlorine on thoroughly representative samples of feathers.

Having made analyses for this trade for some 25 years, I can state with confidence that it is not generally the practice, at any rate in the south of England, to wash feathers or down at all, and, to the best of my knowledge, only two firms actually do so, and these use only cold water.

The result of such washing is to reduce the chlorine to a figure of 6 to 12 parts per 100,000, according to the amount of water used. If I had samples giving figures ranging from 51 to 406 parts per 100,000, I should have reported these as unwashed.

Since the method adopted for rag flock is soaking in cold water only, it does not seem possible for amounts of 51 to 406 parts of chlorine to be left behind, if, as stated, boiling water has been used.

HARLEY F. KNIGHT

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I regret that I overlooked Mr. Knight's contribution on the subject of feathers when I wrote my paper. His figures refer chiefly to imported feathers, which the trade in the south prefer, whereas mine were obtained with all-British feathers. In this connection reference may be made to a passage in a leaflet issued by the Ministry of Agriculture and Fisheries, in which it is stated that home-produced feathers have been found to be more prone to dirt and impurities than imported feathers.*

Presumably, imported feathers are cleaned before shipment. The demand in the north of England appears to be for pillows made from feathers guaranteed "cleaned, washed and sterilised."

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* Advisory Leaflet, No. 252, Ministry of Agriculture and Fisheries. H.M. Stationery Office, Adastral House, Kingsway, W.C.2, 1935. Price 1d. net.

Notes from the Reports of Public Analysts

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

CITY OF BIRMINGHAM

Report of the City Analyst for the First Quarter, 1936

Of the 1467 samples submitted, 65 were bought formally and 1402 informally.

Essence of Peppermint.—This article should consist of a 10 per cent. solution of oil of peppermint in 90 per cent. alcohol. One sample contained the correct amount of oil, but *iso*propyl alcohol was used as the solvent instead of ethyl alcohol. *Iso*propyl alcohol can, of course, be bought at a fraction of the cost of ethyl alcohol owing to the fact that it is not dutiable, and the sample was, in fact, sold at the rate of 1s. per oz. as against 1s. 6d. to 1s. 10d. per oz. charged at other shops on the same day for the genuine article.

There is, of course, no objection to the sale of the cheaper article, if it is made perfectly clear to the purchaser that it is not the genuine B.P. essence, and such an article is, in fact, sold extensively as a flavouring essence. In this instance the article was merely labelled "Essence of Peppermint," which is a strictly B.P. description. The chief chemist of the firm responsible for the sale declared that all assistants had strict instructions to explain the difference between the two articles to customers who were not clear as to which they required, to label the article sold in accordance with its nature, and, in addition, to give verbal notice if the cheaper article was supplied. These instructions were, apparently, not carried out in the present instance, and a circular letter was sent by the chief chemist to all the shops under his control reiterating the precautions necessary in cases of this kind.

In another sample *iso*propyl alcohol was the solvent, and 12 per cent. of oil of peppermint was present instead of 10 per cent., as required by the B.P. The explanation given was that there had been an omission to use the usual slip label explaining the non-official character of the essence.

Milk Jelly Crystals.—A sample was labelled as "Milk Jelly Crystals," and underneath this were the words, "Contains no milk." An article described as milk jelly would be expected by most people to contain milk, and the qualifying statement amounts to a contradiction in terms. In view of the fact that such a disclaimer was actually printed on the packet, however, no administrative action was taken.

H. H. Bagnall

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.

LYSOL SOAP

On May 19th an appeal was heard in the King's Bench Divisional Court (the Lord Chief Justice, Mr. Justice Humphreys, and Mr. Justice du Parcq) from a decision of the stipendiary magistrate of Salford, who had dismissed an information against a firm of soap manufacturers who had been charged under the Merchandise Marks Act with selling soap as Lysol Soap under a false trade description (*cf.* Analyst, 1936, 256).

Mr. W. Gorman, K.C., appearing for the appellant (an official of the Salford Corporation) said that the question was whether the magistrate had power to fix

the standard for lysol in the soap, or whether if there was some lysol present, however little, he could not say that an offence had been committed and that a false trade description had been used. In his (counsel's) submission the word lysol was descriptive, and was the name of a chemical possessing certain characteristics. It was not as though the soap had been called white soap or pure soap. Having been given the name of lysol, it should have disinfectant properties. Unless the quantity of lysol in the soap was sufficient to perform the functions claimed, it was not a true description. The soap was submitted to the borough analyst, who expressed the opinion that it was falsely described. He said that it should contain not less than 1 per cent. of cresols derived from lysol.

Mr. Montgomery, K.C., for the respondents, said that the contention of his clients was that for a toilet soap the soap contained the proper amount of lysol, and that no false description had been applied. There was no evidence on which the magistrate could say that there was so little lysol present that it had no effect on the efficacy or usefulness of the soap, and, unless he found that, he was not entitled to convict.

The Lord Chief Justice, giving judgment, said that the appeal ought to be allowed. The magistrate was manifestly wrong in coming to the conclusion that so long as the soap contained any cresols or lysol he was unable to convict. In other words, that, so long as there was a minute quantity of lysol, there was no false description. He (the magistrate) said that he was not entitled to fix a standard. On the major proposition that so long as the soap contained any cresols or lysol he was not entitled to convict, his Lordship had no doubt that the decision was wrong. The case would go back to the magistrate with a direction to find that the offence charged was proved.

The other Justices concurred.

Department of Scientific and Industrial Research

SULPHUR BACTERIA*

THIS is a comprehensive review of the present state of our knowledge concerning micro-organisms capable of utilising and affecting sulphur and its compounds. The author refers to and draws his information from no less than 143 papers, as well as from unpublished work of his own. Starting from a consideration of the sulphur cycle, he describes the stages which are essentially the work of micro-organisms as follows:

(i) The degradation of proteins to hydrogen sulphide, etc.
(ii) The oxidation of hydrogen sulphide to sulphate; and two sub-cycles:—
(iii) The reduction of sulphur to hydrogen sulphide, and
(iv) The reduction of sulphates to hydrogen sulphide.

The stages (i) and (iii) are disposed of briefly, on account of the non-specific character of the responsible micro-organisms, and the review is concerned mainly with stages (ii) and (iv).

The sulphur oxidising bacteria he divides into three classes:

(*a*) Those oxidising hydrogen sulphide, with deposition of sulphur inside the bacterial cells.
(*b*) Those oxidising hydrogen sulphide, with deposition of sulphur outside the bacterial cells.
(*c*) Those oxidising sulphur and thiosulphates to sulphuric acid.

* *A Review of the Physiology and Biochemistry of the Sulphur Bacteria*, by J. H. Bunker, M.A. Department of Industrial and Scientific Research. Special Report No. 3. H.M. Stationery Office, 1936. Price 9d. net.

The first of these groups, (*a*), he divides into colourless and coloured types—the former chemosynthetic and the latter photosynthetic—the photosynthesis taking place in accordance with the equation:—$CO_2 + 2H_2S \rightarrow H.CHO + H_2O + 2S$, very similar to the ordinary photosynthetic reaction in the presence of chlorophyll: —$CO_2 + 2H_2O \rightarrow H.CHO + H_2O + 2O$, the H_2O being replaced by H_2S and the chlorophyll by the pigments in the sulphur bacteria, which have in fact been shown to be derivatives of chlorophyll-*a*. The variety of conditions described under which these bacteria of his (*a*) group can live and thrive is very remarkable. They have been found in ice-covered pools, and in thermal springs at 80° C., and survive in brine concentration of 30 per cent. They exhibit a wide morphological range, and include the largest bacterium known, *viz.*:—*Hillhousia mirabilis*, which is 20 to 33μ in width and 42 to 86μ in length. The (*b*) and (*c*) types show a fairly wide physiological range, so that species or strains capable of oxidising sulphur and sulphides under a variety of conditions should be procurable. Organisms of this group range from the obligatory autotrophic to the completely heterotrophic. They include aerobic and anaerobic species—species growing at from 0° to 55° C. The optimum reaction of one member of this group, *viz.*:—*Thiobacillus oxidans* is pH = 3 to 4, and the author records actually having kept liquid cultures at pH 0·2, which is equivalent to a 7 per cent. solution of sulphuric acid.

The economic and natural importance of the sulphur-oxidising bacteria is considered:—the preparation of sulphur compounds for assimilation by plants; the elimination of toxic hydrogen sulphide from soil; the solvent action of the sulphuric acid formed on insoluble phosphates; the neutralisation of alkaline soils; decay in stone work, concrete and metals—even to the destruction of pipe lines.

The sulphate-reducing bacteria are shown to constitute a restricted group, of which the outstanding species is the *Vibrio desulphuricans* prevalent in fresh-water muds. The discovery of halophylic and thermophylic types is recorded. Reference is made to the isolation of the enzyme hydrogenase, by which the reduction of sulphate by molecular hydrogen to sulphide has been effected quantitatively in accordance with the equation:—$H_2SO_4 + 4H_2 = H_2S + 4H_2O$. In nature and industry these organisms are shown to be responsible for the blackening of mud; the deposition of calcium carbonate and, perhaps, of metallic sulphides; the occasional tainting of water containing sulphates with hydrogen sulphide on passage through filter-beds; the mass destruction of fish; the discoloration of wood-pulp and paper and the presence of sulphur in petroleum.

There are, in fact, shown to be many problems of theoretical and practical importance in which the sulphur bacteria are concerned.

D. R. W.

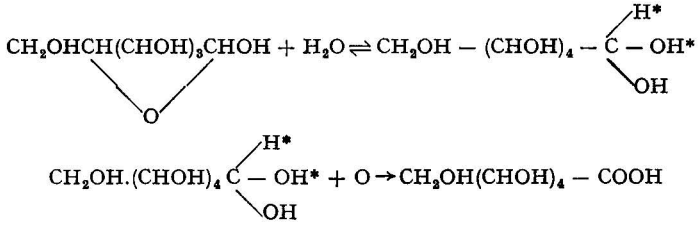
SURVEY OF THE BIOCHEMICAL ACTIVITIES OF THE ACETIC ACID BACTERIA*

THIS monograph opens with a brief historical survey of investigations on the acetic acid bacteria. An account is then given of Kluyver and Donker's theory of microbiological respiration—the process by which the bacterial cells derive the energy necessary for their growth from the substrates in which they grow—from which it would appear that, according to these authors, all respiratory processes of this group are fundamentally the same and consist of catalysis due to the affinity of the protoplasm for certain atoms of the substrate, resulting in a loose combination which brings about a loosening of the bonds of the affected atoms and their subsequent removal in the presence of suitable acceptors. It follows from this theory that it is unnecessary to assume the existence of a separate enzyme for every biological reaction; the existence of hydrolytic, proteolytic and fat-splitting enzymes is admitted, but when dealing with oxidative transformations (or dissimilations

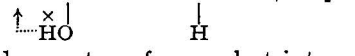
* Chemistry Research Special Report No. 2. K. R. Butlin, B.A. H.M. Stationery Office. 1936. Price 1s. net.

as these authors term them) with which the acetic acid bacteria are concerned, they postulate only a single oxido-reduction producing catalyst. Other theories are mentioned, and the author proceeds to consider in detail, in the light of Kluyver and Donker's theory, the chemical transformations performed by the acetic acid bacteria, these being grouped under the following headings:—(A) The oxidative (aerobic) dissimilation of sugar; (B) Fermentative (anaerobic) dissimilation by acetic acid bacteria; (C) Oxidative dissimilation of alcohols; (D) Oxidative dissimilation of acids; (E) Polysaccharide synthesis, and (E) the oxidative dissimilation of amino-acids.

A. THE OXIDATIVE (AEROBIC) DISSIMILATION OF SUGARS.—According to Kluyver and Donker, the author says, the first degradation product of glucose is gluconic acid, and the reaction leading to the formation of this acid is written:

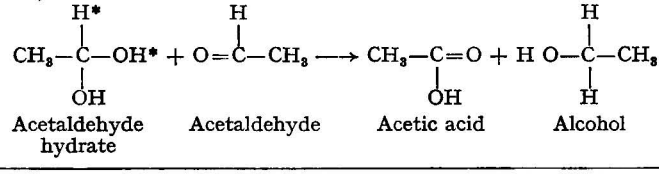


The author suggests that in a somewhat similar manner the following degradation occurs:—gluconic acid → saccharic acid → a β-keto acid—and that the last undergoes decarboxylation to an aldehyde containing one less carbon atom thus:



this being essentially a hydrogen transference but intramolecular. By a series of such catalytic dehydrogenations and decarboxylations ending with CO_2 and H_2O, many intermediate acidic, aldehydic and ketonic products would be formed. It is shown that the following products have been obtained by various workers by the action of acetic acid bacteria on glucose:—gluconic acid, 6-aldehydogluconic acid, 5-ketogluconic acid, succinic acid, lactic acid, glycollic acid, oxalic, acetic and formic acids, carbon dioxide and water. Table I shows the micro-organisms by which these products have been formed and under whose observation. The micro-organisms include *B. Pasteurianum, B. aceti, B. xylinum, B. suboxidans, B. rancens, B. gluconicum, B. orleanse, B. acidosus, B. ascendens, B. Kutzingianum,* and several varieties of *B. Hoskigarki.* These vary widely in their dehydrogenating powers; thus *B. rancens* is very powerful and carries the transformations far, usually to carbon dioxide and water, whilst *B. suboxidans* causes incomplete oxidation. In this section what is known of the degradation of the simpler sugars—glycol, dihydroxyacetone, the tetrose erythrulose and the pentoses—is mentioned.

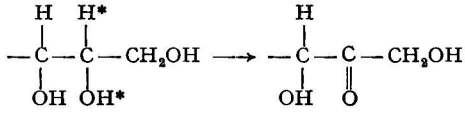
B. FERMENTATIVE (ANAEROBIC) DISSIMILATION.—Reference is made to the work of Neuberg and Simon, who found that *B. ascendens* formed alcohol and carbon dioxide from glucose anaerobically; to the formation of acetic acid and ethyl alcohol from acetaldehyde by three acetic acid bacteria, as recorded by Neuberg and Windisch; and to the Cannizaro reaction by means of which it is thought that this takes place, viz.:



Acetaldehyde hydrate | Acetaldehyde | Acetic acid | Alcohol

* Indicates activated hydrogen atom.

THE OXIDATIVE DISSIMILATION OF (C) ALCOHOLS AND (D) ACIDS.—It is shown that methyl, propyl, butyl and amyl alcohols are decomposed, with the formation of corresponding acids, or acetone in the case of *iso*propyl alcohol. Account is given of the action of acetic acid bacteria upon many polyhydroxy alcohols, and it is interesting to note that, as a general (but not universal) rule, the stereochemical configuration favourable for dehydrogenation is that in which the hydroxyl of the third carbon atom is on the same side of the chain as the hydroxyl of the secondary alcohol group in the β-position, thus:



* Indicates activated hydrogen atom.

The production of dihydroxyacetone is specially mentioned as of importance in the synthesis of resins.

The action of the acetic acid bacteria on the following monobasic aliphatic acids is shown:—formic, acetic, butyric and *iso*butyric; and upon the polyhydroxy acids:—oxalic, malonic, succinic, glutaric, fumaric and aconitic.

The sections on polysaccharide synthesis (E) and oxidative dissimilation of amino-acids (F) can be referred to only very briefly in this summary. The production of cellulose by *B. xylinum* from glucose, fructose, glycerol, sorbitol, etc., and the identification of the membranes produced as cellulose is of special interest. The effect of the acetic acid bacteria on amino-acids is shown to be (*a*) deamination, (*b*) substitution of OH for NH_2, and (*c*) decarboxylation.

Several lines of further research are suggested, and a bibliography of 86 references is appended.

D. R. W.

The National Physical Laboratory

REPORT FOR THE YEAR 1935

THE Report opens, as usual, with the Report of the Executive Committee, in which there are sympathetic notices on the deaths of Sir Richard Glazebrook on December 15th, 1935, and of Sir Joseph Petavel, Director of the Laboratory, on March 31st, 1936.

INTERNATIONAL CONFERENCE ON ELECTRICAL UNITS OF MEASUREMENTS.—In September, 1935, the International Committee of Weights and Measures, at a meeting held in Paris, decided that the substitution of the absolute system of electrical units for the international system shall take place on January 1st, 1940. For most engineering applications, however, the old values will be sufficiently close for no change, even of a numerical nature, to be required. The following table gives a provisional list of the ratios of the international units to the corresponding practical absolute units, taken to the fourth decimal place:

1 Ampere	international	= 0·999, 9	Ampere	absolute
1 Coulomb	,,	= 0·999, 9	Coulomb	,,
1 Ohm	,,	= 1·000, 5	Ohm	,,
1 Volt	,,	= 1·000, 4	Volt	,,
1 Henry	,,	= 1·000, 5	Henry	,,
1 Farad	,,	= 0·999, 5	Farad	,,
1 Weber	,,	= 1·000, 4	Weber	,,
1 Watt	,,	= 1·000, 3	Watt	,,

PHYSICS DEPARTMENT: HEAT DIVISION.—The experiments on the ratio of the specific heats of gases at high temperatures by the stationary-wave method have been continued. The preliminary results for carbon dioxide agree well with those calculated from spectroscopic data, which predict a ratio of 1·17 at a temperature of 900° C.

In connection with the International Temperature Scale, the ingot technique that was used for the freezing-point of platinum has proved equally satisfactory for palladium, for which the latest laboratory determination of the freezing-point confirms, within the estimated limits of error, the value 1,555° C. adopted in the specification of the International Temperature Scale. Progress has been made in the development of black-body radiators of exceptional uniformity and constancy of temperature.

FOOD INVESTIGATION PROBLEMS.—Various investigations have been pursued for the Food Investigation Board. The heat transfer from a "gilled" pipe in an air-stream is approximately the same under like conditions as that for a plain pipe of the same surface area per unit length. Measurements have been carried out on the dependence of the rate of total evaporation on the size of a moist surface, whether spherical, cylindrical or plane, in a wind stream. In the evaporation met with in the cold-storage industry the thermal aspect of the matter is important, since latent heat is necessarily absorbed in the process. A study has also been made of the convective heat transfer from plane surfaces in free air, since convection is another process by which heat is extracted from stored foodstuffs. It has been found that in an air-stream evaporation and convection follow analogous laws.

The viscosities of certain of the liquids which have more recently come into use as refrigerants have been measured over a range of temperature down to − 15° C. by a falling-plug method, and the effect of impregnation with carbon dioxide (which is frequently used in the cold storage of fruit and meat) on the thermal conductivity of certain building and insulating materials is under study. The laws governing the discharge of air from ports in the sides of a trunkway, such as is used for distributing cold air in stores and in the holds of ships, have been examined both theoretically and experimentally. The agreement between the two methods was very satisfactory.

The air-conditioning of museums, libraries and picture galleries presents special problems, in connection with which experiments have been carried out for H.M. Office of Works. These experiments included the determination of the moisture-content of vellum at different humidities, and an examination of the rate of response when the humidity of the surrounding air was changed.

RADIOLOGY DIVISION.—The X-ray diffraction method has been applied to a detailed survey of the structural changes occurring in metal wires under longitudinal tension.

In continuation of the work on the relation between hardness and lattice distortion, studies are being made of electro-deposited chromium, which gives abnormally diffuse diffraction lines when deposited under suitable conditions.

Paint Materials.—In co-operation with the Research Association of British Paint, Colour and Varnish Manufacturers, various X-ray investigations of materials have been made. In studies of various lead oxides it has been shown that litharge (PbO) can exist in two crystalline forms, one of which is orthorhombic and the other tetragonal. By varying the method of preparation one or other of these forms, or a mixture of the two, may result. Studies of a series of red lead preparations prove that red lead (Pb_3O_4) has its own characteristic X-ray pattern, which is different from that of either PbO or PbO_2. When the results of a chemical analysis of a red lead by the estimation of its equivalent PbO_2 content show that the proportion of PbO_2 is less than 33·3 per cent. (atomic), then the X-ray pattern indicates that the red lead is a mixture of Pb_3O_4 and PbO. When the percentage reaches 33·3 per cent., the PbO lines disappear from the X-ray pattern. Attempts to

correlate the setting properties of red lead with the structure, as revealed by X-ray methods, have so far led to the conclusion that the non-setting red leads show better defined diffraction lines and are characterised by more fully developed crystals. There are indications that the quality of the red lead pattern depends to some extent on the crystal nature of the litharge used in its production.

Other materials, which are still under investigation, include Prussian blues and a fatty acid (elaeostearic) glyceride. As regards the Prussian blues, which vary in method of manufacture and in properties, the X-ray evidence suggests that they all contain a common component of, as yet, undetermined composition, but this conclusion is not fully confirmed. Electron diffraction methods are also being used in connection with this problem. With regard to the β-elaeostearic glyceride, the results of the preliminary work suggest that two forms with different melting-points exist as allotropic crystal modifications.

Carbon Blacks.—An X-ray study of the structure of various carbon blacks is in progress. The object of the investigation is the determination of the structures most suitable for various applications, particularly in the rubber industry. The X-ray diffraction patterns obtained up to the present indicate that the main difference between the various specimens examined is in the grain size, which can vary over wide limits. Thus carbon blacks, such as the gas black used in the ink and varnish trade, and a standard rubber gas black give only diffuse haloes, suggesting an almost amorphous structure. Lamp-black gives diffraction lines which, although weak, are sharp and occur on a heavy background, showing that this carbon consists of a mixture of amorphous and crystalline material. These results are in general agreement with independent measurements of grain size made by other methods.

X-Ray Studies of Tooth Structure.—From the radiographic investigation of the structure of teeth, it is tentatively suggested that a good enamel should satisfy the following conditions: (*a*) it should show a large amount of well-developed fibre structure; (*b*) the fibre axis should have a special position; and (*c*) the calcification should be normal.

Optics.—Work on the tabulation of quantities relating to the properties of simple lens combinations has been continued.

Colour Measurement and Standardisation.—A simplified colorimeter has been constructed and has proved very successful; the instrument will be produced commercially. Work has been continued on the problem of eliminating the personal error of observers in colorimetry. One of the methods investigated was to modify the characteristics of each individual observer by means of a correcting filter, placed in front of the eye, through which all colour measurements are taken. The most suitable constitution for this filter was derived from measurements on a series of colours of those types for which the errors are likely to be greatest, the values for the normal observer being obtained by calculation from spectrophotometric measurements. This method met with only partial success. With certain observers practically complete correction was obtained, but with others the departures from normal were such that a satisfactory degree of correction could not be achieved.

An alternative method of attacking this problem has been under consideration. The errors in question arise from dissimilarity in energy distribution between the stimulus to be measured and the matching stimulus. This dissimilarity can be reduced by filling the gaps in the matching stimulus by means of additional components. An instrument involving the use of three additional stimuli, suitably spaced in relation to the unitary stimuli of the working system, has been designed, and is at present under construction.

Infra-red Wave-length Determinations.—During the year further measurements have been made on the transmission of crystalline and fused quartz, and on the emission and absorption spectra of carbon dioxide. Considerable trouble has been

experienced with the galvanometer system, due to mechanical disturbances, and this has necessitated further experiments to secure steadier conditions; these have not reached completion. A description has been prepared of the infra-red spectrophotometer.

Radiation Measurements.—Attention has been given to the problems arising from the calibration of instruments for measuring radiation. Owing to the failure of attempts to establish satisfactory correlation between measurements with solar radiation and that from artificial sources, it would appear that solar radiometers can be calibrated only in the summer months, when natural radiation of suitable intensity is available.

METALLURGY DEPARTMENT.—An account of the methods adopted for the preparation of iron of exceptionally high purity has been published, and some of the physical properties of such iron have been determined. Certain anomalies in the magnetic properties and the transformation points call for further investigation.

The examination of oxide films on liquid and solid metals has been continued, constant use being made of the electron diffraction method of investigation. The rate of oxidation of liquid tin in oxygen varies greatly in different experiments, and it is suggested that the orientation of the crystals composing the oxide film is a determining factor.

Work on the determination of oxides in iron and steel has been continued both by the vacuum fusion and the iodine methods. The technique of the former has been improved, so that temperatures up to 2000° C. can be attained.

Other investigations include work on the light alloys of aluminium, and a study of the structural changes in mild steel, Swedish iron, ingot iron and carbonyl iron under conditions of creep *in vacuo*.

Dental Amalgams and Alloys.—The investigation of dental amalgams has led to the conclusion that, in order to obtain an amalgam which will give only the desired expansion during setting, the composition of the alloy to be mixed with mercury must lie within very narrow limits, the expansion being too great when the proportion of tin is diminished, whilst contraction occurs when it is increased. The constitution of the amalgams over the important range of composition has been determined, and the changes in dimensions on setting have been correlated with the reactions thus indicated, which, however, are never complete under the conditions of use.

A dental alloy containing 26 ± 0·3 per cent. of tin, 5 per cent. of copper and 69 per cent. of silver should prove one of the best in practice; zinc may replace copper up to not more than 1·5 per cent.

The presence of beryllium was found to be detrimental to silver-tin dental alloys.

The Report also includes the Reports of the Superintendents of the Electricity, Radio, Metrology, Engineering and Aerodynamics Departments and of the William Froude Laboratory.

Connecticut Agricultural Experiment Station

REPORTS ON FOOD AND DRUG PRODUCTS, 1934

THIS is the 39th Report of the Station on food products and the 27th Report on drug products. The Station's interest in foods, their composition and possible adulterations began almost at the date of its founding in 1875. In 1877 the Station announced the services that it was prepared to render for the use and benefit of citizens of the State. In 1886 the General Assembly passed an Act to prevent and punish fraud (in foods) and provided that the Dairy Commissioner might have the samples analysed by the Experiment Station or by a State chemist. In 1895 a general food law was passed, and this required the Experiment Station to collect and examine samples and to publish an annual report thereon.

The Connecticut Station was the first Agricultural Experiment Station in U.S.A. to be delegated by act of legislature to exercise control over foods as regards fraud and adulteration. Other State experiment stations were later similarly delegated: Kentucky in 1898, North Dakota and Wyoming in 1903, and Maine in 1905.

In 1907, after passage of the Federal Food and Drugs Act, the State law of 1895 was revised to conform to the Federal Act, and accordingly its scope extended to include drugs. This Act empowered the Dairy and Food Commissioner and the Connecticut Agricultural Experiment Station to take samples for inspection purposes, but the Commissioner was charged with enforcement. It differed from the preceding Act in that it designated a definite enforcing authority.

During the year under review 1229 samples of food were examined, including 559 milks and milk products, 138 beverages, and 114 of sweet pickles. Of the 188 samples of drugs examined, 72 were adulterated or incorrect.

OLIVE OIL AND OTHER EDIBLE OILS.—One of the most difficult problems in the control of adulterated olive oil is that presented by its sale through "bootleg" channels. Deliveries are made without invoice or other papers incidental to the sale, and the packages bear no identification as to the packer. When questioned, the retailer does not know or "cannot remember" from whom he purchased.

An objectionable feature in the marketing of edible vegetable oils, other than olive oil, is the practice of packing them in containers which simulate the general style, dress and design of those in which genuine olive oil is packed. Descriptive names and legends such as "olio," "olio finissimo," "Lucca" and other Italian place names are commonly used in labelling products consisting largely, or entirely, of domestic oils.

In the later months of 1934, owing to advances in the price of cottonseed, maize and other domestic oils, imported sunflower oil came into extensive use as a substitute for these products.

During the year a joint committee of federal control officials from the States of New Jersey, New York and Connecticut studied the question of the labelling of edible oils, and made the following recommendations *inter alia*:

1. That the words "Oil" or "Olio" should be used only in conjunction with the distinctive name of the kind, or kinds, of oil present.
2. That the terms "Salad Oil," "Cooking Oil," "Vegetable Oil," etc., should not be used in naming the kinds of oils contained in the package, but that the particular kinds of oils should be declared with their common names.
3. That, in the case of mixtures of oils, a complete, plain and conspicuous statement of composition immediately follow the brand designation.
4. That the words "Italy," "Italia," "Lucca" or other foreign provincial names and names of prominent Italian persons or their pictures be not used on labels of mixed oils, one or more of which are of domestic origin.

5. That the pictures of olive trees, or other trees or shrubbery tending to create the impression that they are olive trees, Italian country scenes with pictures of Italian peasants, coats of arms, medals, coins, etc., have no place in the labels on these products and should be prohibited.
6. That the terms "Virgin," "Vergine," "Pure," "Purio," "First Pressed" and the like should be eliminated from these labels.
7. That the use of superlative terms as "Fino," "Vera," "Superiore," "Superfine," "Prima," etc., is not descriptive of a blend of oils and has no place on such labels.
12. That, when artificial colour or flavour or both are used to simulate olive oil, the product should be labelled as an imitation. The words "olive oil" should be in no larger type than the word "imitation" and should immediately follow that word. A statement of composition should be used in conjunction with the designation "imitation olive oil" and should be fully informing, such as "cottonseed oil, 85 per cent.; olive oil, 15 per cent.; artificial colour and flavour."

Of 100 samples officially examined, very few were above criticism as to labelling. Corrective action was taken by the Dairy and Food Commissioner by means of interviews and prosecutions, and distinct improvement has been brought about.

ICE CREAM, ETC.—Ice cream of legal standard must contain not less than 10 per cent. of milk-fat, except fruit and nut ice creams, for which the minimum fat content is 8 per cent. To guard against undue increase in volume, known as "swell" or "overrun," in the process of freezing, the statute provides that the content of food solids shall not be less than 1·6 pounds per gallon.

Samples taken from bulk cannot be judged as to solids per gallon, because there is no way of conveniently determining the exact volume of the samples. Samples submitted in unit packages of declared volume are judged according to the declared volume, and solids per gallon are estimated on that basis.

Nineteen samples were examined in 1934, and all met or exceeded the minimum of 10 per cent. of milk-fat. Ten of them were in packages of declared volume, and these contained from 1·7 to 2·4 pounds of solids per gallon and thus met the statute requirement.

The article known as "frozen custard" is of the same general character as ice cream, but usually of lower fat-content. Regulations require that such products be labelled to show the percentage of fat present when not meeting the fat-standard for ice cream. Correctly speaking, a "custard" is an egg product, and "frozen custard" should be classed as "French ice cream," which is made with eggs. Under the laws and regulations in many States, frozen custard is required to meet the specifications laid down for French ice cream, but efforts so to classify that article in this State have been opposed by those interested in the manufacture and sale of the product.

MATÉ.—The shrub is not adapted to the climate of North America, although a related species, *Ilex cassine*, is grown in some of the Southern States.

Analyses of two commercial brands of maté and, for comparison, two samples of cassina are given in the subjoined table.

Preparation	Moisture Per Cent.	Pet. spt. extract Per Cent.	Hot water extract Per Cent.	"Tannins" Per Cent.	Nitrogen Per Cent.	Crude fibre Per Cent.	Caffeine Per Cent.	Ash, per Cent.			
								Total	Water-soluble	Acid-insol.	Sol. P_2O_5
Yerba maté ..	5·29	4·00	45·70	7·59	2·37	—	1·32	5·98	2·90	0·19	—
Joyz maté ..	7·80	5·98	43·45	7·90	2·31	—	1·30	7·70	2·81	0·31	—
Cassina, black	3·15	1·68	31·00	—	2·25	14·13	0·69	6·00	1·71	1·09	0·03
Cassina, green	3·68	1·98	40·00	—	2·30	12·29	0·38	6·00	1·72	1·40	0·14

Woodward and Cowland (ANALYST, 1935, **60**, 135) have investigated the so-called tannin in maté. They conclude that, although the usual methods give values for this constituent that are of about the same magnitude as those for tea,

there is no true tannin in maté. Evidence was obtained indicating the presence of caffetannin or a closely-related pseudo-tannin.

It will be noted that the amount of caffeine, to which the stimulating effects of the beverage are largely due, is of about the same magnitude as in coffee. Caffeine is higher in commercial teas, and generally ranges from 1·9 to 3·3 per cent. Tea will yield from 35 to 40 per cent. of hot-water extract. The two samples of maté examined yielded somewhat more, 43·5 to 45·7 per cent.

SUCRATE OF LIME IN CREAM.—Thickening with sucrate of lime was suspected in a number of cases. Tests on prepared samples were made by various methods. The Elsdon procedure (ANALYST, 1918, **43**, 292) on the cream direct and on the uranium acetate serum resulted in dark brown colours in all cases when evaporation over steam was employed. The following technique, however, was found to distinguish between the treated and the untreated samples.

Modified Baier and Neumann Test.—To 25 ml. of cream add 25 ml. of water and 10 ml. of 5 per cent. uranyl acetate solution and filter. Take 10 ml. of the filtrate and mix with 2 ml. of saturated ammonium molybdate solution and 8 ml. of 1 : 7 HCl. Heat for 5 minutes at 80° C. and filter. The filtrate was blue in both the treated and untreated samples, but with the pure cream the colour was much less intense than the shade of Prussian blue used for comparison and produced by a mixture of 1 ml. of 0·1 per cent. ferric chloride, 20 ml. of water, 5 drops of 10 per cent. sulphuric acid and 2 drops of *N* potassium ferrocyanide.

Resorcinol Test.—To 3 ml. of the uranyl acetate filtrate add 0·1 g. of resorcinol and 0·3 ml. of 3 *N* hydrochloric acid. Place 0·5 ml. of this mixture in a depression of a porcelain spot-plate and leave at room temperature in a desiccator overnight, or until dry. A pronounced pink colour was produced in the calcium sucrate cream, but the pure cream developed no pink colour.

Two samples of commercial cream gave positive tests by both of the above procedures. The results were negative or inconclusive with the other samples. The fat-content of the samples giving positive tests was 34·5 per cent. in each, and the content of calcium oxide was 0·123 and 0·124 per cent.

MAPLE BUTTER.—There is no official definition of maple butter. The product submitted appeared to be made from maple sugar and other sugars and gelatin. Partial analysis gave the following results:—moisture, 20·06; total ash, 0·35; water-soluble ash, 0·26; water-insoluble ash, 0·09; protein, 0·69 per cent. Winton lead number, 0·57; gelatin present.

British Guiana

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1935

IN his Annual Report the Government Analyst (Mr. Kenneth Wallis) gives an outline of the work done for 22 Government Departments. Of the 6801 samples examined, 1924 were submitted by the Inspector-General of Police, 1538 by the Comptroller of Customs, and 2371 by the Medical Departments.

WINES, LIQUEURS, CORDIALS.—On importation into the Colony the duty on wines is dependent on whether they contain not more than 26, 30, 35 or 42 per cent. of proof spirits, the higher the percentage of alcohol the greater the duty. This refers only to still wines, whether in bottle or in bulk, sparkling wines being required to pay a higher rate of duty. Four hundred and forty-four samples of wine and three samples of bitters and cordials were examined on importation. During the year the manufacture of local wine increased considerably, and the Excise officers submitted 215 samples.

Under the Food and Drugs (Consolidation) Ordinance, Cap. 102, wine, to be sold as such, must have, among other requirements, a minimum of 13 and a maximum of 42 per cent. of proof spirits. The Bitters and Cordials Ordinance, Cap. 109, provides, among other stipulations, for fermented liquors to be sold as "Sweets" if they contain more than 4 and less than 26 per cent. of proof spirit.

AERATED WATERS.—One hundred and fifty-five samples of aerated waters and materials were analysed. As the control of the local aerated water factories is under this Department, they have to be inspected with a view to seeing that they comply with the conditions for operating laid down by the Governor in Council. There are at the present time thirty-two of these factories on the register, and they are widely distributed in the Colony.

The use of saccharin in sweetened aerated waters is prohibited. Frequent visits have been made to these factories, and samples of syrup were taken. The general standard of cleanliness has greatly improved as a result of the increased number of visits of inspection.

TOBACCO.—All of the tobacco which is examined from the Customs Department consists of the "black fat" leaf variety. Manufactured cigars, cigarettes, tobacco and snuff, etc., pay specific rates of duty and have none of the restrictions which are placed on the leaf variety. The latter must contain less than 38 per cent. water. Formerly they were also examined for the percentage of oil, a maximum of 6 per cent. of which was allowed, but this is no longer required. Two hundred and five samples on arrival in the Colony were examined for the Customs.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Reducing Sugars with the Cupro-alkali Metal Carbonate Solution. II. A Modification of Pellet's Solution. Chang Y. Chang and H. A. Schuette. (*Trans. Wisconsin Acad. Sciences, Arts and Letters*, 1935, **29**, 381–388.)—The modified form of Pellet's solution (C) consists of two parts, (A) and (B), mixed in the volume ratio 1 : 4 immediately before use. (A) contains 343·5 g. of $CuSO_4.5H_2O$ and 34·35 g. of ammonium chloride; (B) contains 216·25 g. of sodium potassium tartrate and 283·5 g. of anhydrous sodium carbonate per l. As (A) is not photo-sensitive, no blank determination on (C) is necessary. The optimum conditions for use are:—(i) Time, 45 minutes; (ii) temperature, 90° C.; (iii) reagent, 20 ml.; (iv) sugar solution containing not more than 4 mg. of reducing sugar per ml.; (v) dilution of reaction mixture with water to 80 ml. Stoppered flasks should preferably be used for the reaction, to maintain the original volume and eliminate temperature fluctuations at the surface.

When Fehling's solution is replaced by (C) for the determination of reducing sugars in the presence of sucrose, the latter has been found to be passive under the above optimum experimental conditions. No cuprous oxide was formed in two 80-ml. reaction mixtures containing (*a*) 80 mg. and (*b*) 2 g.; of sucrose. In two series of experiments, sucrose was mixed with dextrose, laevulose, and an equal mixture of these, to the extent of 5 per cent. and 50 per cent. in the respective series. No significant increase in copper equivalent was obtained. Results for

maltose were similar; lactose gained slightly in reducing power when it formed only 17 per cent. of the mixture. This passivity towards sucrose is considered to be a unique property of the reagent. E. B. D.

Composition of Hungarian Apple Juice. S. M. Finály. (*Z. Unters. Lebensm.*, 1936, **71**, 322–323.)—Commercial preparations of fruit juice now available in Hungary include the juices of apples, grapes, raspberries, pears, and other fruits. The method of preparation is as follows:—The fruits are washed and minced, and the juice is expressed, and clarified with an enzymic preparation which precipitates the pectic substances. After sedimentation or filtration, the juice is sterilised at 72° to 74° C., and sealed up in bottles which have previously been washed with a solution of sulphur dioxide. The products appear to be quite stable and show no indication of fermentation when the bottles are kept at room temperature for one or two days after being opened. The average values for three of these apple juice products are compared below with the average values found by König for the natural juice of apples (*Chemie der menschlichen Nahr- und Genussm.*, Vol. I, B, 1923). (The figures quoted from König's work for total sugar, tannin, and alkalinity number are single values; the remaining figures are average values.)

	Sp.gr. at 15° C.	Soluble matter Per Cent.	Insoluble matter Per Cent.	Total sugar Per Cent.	Invert sugar Per Cent.	Sucrose Per Cent.	Total acid (malic) Per Cent.	Tannin Per Cent.	Ash Per Cent.	Alkalinity of Ash	Alkalinity number
Average values for 3 commercial samples	1·0491	13·31	0	10·29	9·38	0·83	0·62	0·02	0·26	2·6	10·3
Average of König's values for apple juice	—	11·98	2·56	11·88	8·01	1·63	0·60	0·07	0·30	2·9	10·2

The results show that the chemical composition of the commercial products resembles that of apple juice very closely. As was to be expected, the processing removes the greater part of the tannin and the whole of the insoluble matter, and, although the ash-content is slightly lower, there is little diminution in its alkalinity. A. O. J.

Effect of Certain Ingested Fatty Oils upon the Composition of Cow's Milk-fat. T. P. Hilditch and H. M. Thompson. (*Biochem. J.*, 1936, **30**, 677–691.)—Comparisons have been made of the component acids in milk-fats from cows which have received a normal winter diet and from cows which have had, in addition, cod-liver, linseed and rape oils. The effect of cod-liver oil was very marked, the lower saturated acids of the milk-fats being reduced to half the normal content, whilst the proportion of oleic acid was increased, and 5 to 7 per cent. of highly-unsaturated C_{20-22} acids were present. The polyethenoid unsaturation in the C_{18} acids was not more than normal, and palmitoleic acid was not appreciably absorbed from the oil. When linseed oil was fed to the cows, the proportion of oleic acid was increased, but linolenic acid was not detected and only small amounts of linolic acid were found. The unsaturation of the C_{18} acids and the amount of the lower saturated acids were normal. The effect of rape oil was similar to that of linseed oil, but small amounts of erucic glycerides were found in the milk-fats. The relationship between the fully-saturated glyceride-content and the proportion

of total saturated acids was normal in every instance. Some of the highly-unsaturated C_{20-22} glycerides from cod-liver oil (but not the palmitoleic or the linolenic and linolic acids of linseed oil) pass into the milk-fats, and it is suggested that selective adsorption of these highly-unsaturated compounds by the enzymes responsible for the formation of the fats typical of cow's milk retards the normal function and causes the observed effects. S. G. S.

Composition of Olive Oils from the Islands of Rhodes and Cos. V. Brandonisio. (*Chim. e Ind.*, 1936, **18**, 14–16.)—References are given to several papers in which it is shown that in olive oil, contrary to seed oils, the percentage of linolin is greater in oils from warm regions than in those from cooler countries; it is possible, however, that olive-kernel oil may be affected by climate in the same way as other seed oils. In the present researches oils from Arcangelo, Afando, Alaerma, Cos, Peveragno, and Rhodes were studied. In these oils the refractive index, the saponification value and other constants were normal, but the iodine values of the oils and of the liquid fatty acids were high, the former varying from 84·2 to 88·9, and the latter from 101·6 to 104·6. The percentage composition is given in the following table:

Locality	Olein	Linolin	Palmitin	Stearin	Myristin
Arcangelo ..	67·80	10·56	19·41	—	0·91
Afando	66·60	13·14	18·48	—	0·35
Alaerma ..	67·63	12·33	18·16	—	0·57
Cos	67·96	13·52	16·87	—	0·39
Peveragno ..	68·60	10·49	18·80	—	0·81
Rhodes	68·58	10·30	19·40	0·26	—

In composition, these oils are very similar to several varieties of oils from Apulia and Sicily, probably owing to the similarity of the climates. E. M. P.

Optical Rotation and Unsaponifiable Matter of Olive Oils. W. Ciusa. (*Chim. e Ind.*, 1936, **18**, 13–14.)—Pure expressed olive oils cannot be distinguished from extracted ("refined") oils by the optical rotation, the values for which come within the same range (+0·20 to +0·60; exceptionally +0·15 to 0·90 Ventzke degrees). However, on treatment with active charcoal, the rotation of expressed oils is reduced almost, if not quite, to zero, whilst that of "second" refined oils decreases only slightly; two samples of "first" refined oils behaved in the same way as expressed oils. The changes in the optical rotations and in the amounts of unsaponifiable matter in olive oil during the process of refining were as follows:

	Unsaponifiable matter Per Cent.	Optical rotation Ventzke
(1) Crude "disulphide" oil (filtered through filter-paper)	1·61	—*
(2) Washed with water and treated with 1·5 per cent. of conc. sulphuric acid	1·57	+ 0·97
(3) Neutralised with caustic soda to 20–25 per cent., and separated from the soap	2·25	+ 0·87
(4) Decolorised with charcoal ("Klarit")	1·55	+ 0·75
(5) Deodorised with super-heated steam	2·05	+ 0·60
(6) Finished product	1·47	+ 0·45

* The sample was too opaque for its optical rotation to be read, but it was of the same order as that of (2).

E. M. P.

New Method for the Detection and Determination of Diacetyl. J. Pien, J. Baisse and R. Martin. (*Ann. Falsif.*, 1936, **29**, 204–225.)—The basis of the method is the condensation of ketones with amines. With α-diketones, amines with the amino groups attached to adjacent carbon atoms are required, in order that both CO groups may react with the NH_2 groups. As the reaction is colorimetric, an orthodiamine is necessary. *Detection.*—To 10 ml. of the solution to be tested, 0·5 ml. of a 1 per cent. aqueous solution of *m-p*-toluylene-diamine is added in a test-tube and shaken. Ten ml. of concentrated sulphuric acid are then run slowly down the side of the tube, from a pipette. A yellow colour, due to quinoxaline, is formed. The liquids are mixed by slanting the tube, and the colour reaches a maximum on standing for about an hour. The colour is quite appreciable with 10 p.p.m. of diacetyl. A blank test should be made, but the authors have never obtained a colour in the absence of diacetyl. *Determination.*—The solution to be tested is compared colorimetrically with a standard solution prepared from diacetyl or potassium dichromate solution of a colour which matches this. If diacetyl is used, the initial concentration should be 1 : 5000. A sample giving a more intense colour than this is diluted; with a paler colour, the standard solution is diluted, until the colours are of approximately the same depth, before comparing the two liquids. The diacetyl used for the standard solution must be chemically pure, and the diluted solutions must be re-made, and the reaction carried out for each test. A solution of potassium dichromate, which corresponds in colour with that from the diacetyl, is therefore preferable. It is made by taking x ml. of a 1 per cent. solution and diluting it to 200 ml. with distilled water. The colour, using different values for x, is compared with that of the solution to be tested. The following table is given:

Strength of diacetyl solution	Value of x
1/1,000	6·7
1/2,000	5
1/5,000	3
1/10,000	1·9
1/20,000	1
1/50,000	0·50

To determine diacetyl in foods, the volatile matter is steam-distilled from 1 kg. or 1 litre after preliminary heating on a water-bath. The first two portions of 50 ml. of distillate are collected. From each of these, exactly 10 ml. are redistilled. The above determination is made on each 10-ml. portion.

E. B. D.

Hydrocarbon removed in the De-odorisation of Olive Oil. H. Marcelet. (*Ann. Falsif.*, 1936, **29**, 231–233.)—Crude olive oil contains 0·1 to 0·2 per cent. of oily matter which is removed in refining with superheated steam to deodorise the oil. The constants of the oily matter removed differ greatly from those of the olive oil. In one instance they were:—sp.gr. at 15° C., 0·9124; oleorefractometer reading at 22° C., 14; acidity (as oleic acid), 11·15 per cent.; saponification value, 162; iodine value (Hanus), 89; unsaponifiable, 7·67 per cent.; phytosterol, 0·08 per cent. The unsaponifiable matter had the following constants:—sp.gr. at 15° C.,

0·8755; n_D^{16} 1·4910; iodine value (Hanus), 173; molecular weight (cryoscopic method), 289. It had an aromatic odour, was soluble in benzene, ether and petroleum spirit, and slightly soluble in cold alcohol. All its reactions were those of hydrocarbons. Four fractions were obtained from it by fractional distillation *in vacuo* (5 mm. of mercury); these were separated into four liquids and three solids, and their constants determined. The results, which are tabulated, show the products to be saturated and unsaturated hydrocarbons containing from 13 to 28 carbon atoms in the molecule. E. B. D.

Chemical Assay of Ergot. C. H. Hampshire and G. R. Page. (*Quart. J. Pharm.*, 1936, 9, 60–74.)—The alkaloids of ergot can be completely extracted with ether in the continuous-extraction apparatus of the British Pharmacopoeia, 1932. Glyoxylic acid as a reagent for the colorimetric determination of these alkaloids has no advantage over *p*-dimethylaminobenzaldehyde. Although ergotoxine and ergometrine in aqueous solution may be separated by extraction with carbon tetrachloride or amyl ether, this process is unsatisfactory for the assay of ergot on account of the formation of emulsions. The following method, in which the water-soluble alkaloids are separated from the water-insoluble alkaloids by shaking out an ethereal extract with water, is suggested. Ten g. of ergot in moderately fine powder (44 to 60) are extracted with petroleum spirit (b.p. 40° to 50° C.) in a continuous-extraction apparatus until the fat is completely removed. The extracted drug is dried at a temperature not exceeding 40° C., and transferred to a porcelain dish. Sufficient ethyl ether is added to form a semi-liquid mass, followed by 2 ml. of strong solution of ammonia, and the whole is stirred with a glass rod. When most of the ether has evaporated, the residue is returned to the continuous-extraction apparatus and extracted for about five hours with 100 ml. of pure ether. The ethereal solution is then filtered through a small filter, and the flask and filter are washed with small volumes of ether until 120 ml. are obtained. For the total alkaloids, 60 ml. of the ethereal solution are shaken successively with 10, 10, 5, and 5 ml. of a 1 per cent. aqueous solution of tartaric acid. The acid solutions are mixed and warmed gently in a current of air, cooled and diluted to 30 ml. with water. One ml. of this solution is mixed with 2 ml. of dimethylaminobenzaldehyde solution (0·125 g. of dimethylaminobenzaldehyde in 65 ml. of sulphuric acid and 35 ml. of water to which 0·1 ml. of ferric chloride solution (B.P.) is added). To another 2 ml. of the dimethylaminobenzaldehyde solution 1 ml. of ergotoxine ethane sulphonate solution (0·012 per cent. in 1 per cent. tartaric acid solution) is added. After five minutes the colours of the two solutions are compared in a colorimeter. For the water-insoluble alkaloids, the remaining 60 ml. of the ethereal solution are extracted with successive quantities of 20 ml. of water made faintly alkaline to litmus with ammonia, until 1 ml. of the aqueous layer gives no blue colour when mixed with 2 ml. of the dimethylaminobenzaldehyde solution. The ethereal solution is now shaken with successive quantities of 10, 10, 5, and 5 ml. of the 1 per cent. tartaric acid solution. These extracts are united, warmed gently in a current of air, cooled and diluted to 30 ml., and this solution is used for comparison with the ergotoxine solution as before. By subtraction of the water-insoluble alkaloids from the total alkaloids, the water-

soluble alkaloids (as ergotoxine) are obtained, and, if this value is multiplied by 0·538, the amount of ergometrine (including any ergometrinine) is found. The recovery of added amounts of alkaloids in duplicate determinations was satisfactory. S. G. S.

Determination of Camphor as 2-4.Dinitrophenylhydrazone in Concentrated and Dilute Tinctures. M. M. Janot and M. Mouton. (*J. Pharm. Chim.*, 1936, **128**, 547–549.)—A modification of Hampshire and Page's method (*Quart, J. Pharm.*, 1934, **1**, 558) is recommended for the determination of natural or synthetic camphors. Two ml. of the camphor tincture are diluted with 13 ml. of 90 per cent. alcohol in a 300-ml. conical flask, and 85 ml. of the reagent (1·25 g. of 2-4.dinitrophenylhydrazine in a mixture of 10 ml. of water and 10 ml. of conc. sulphuric acid, made up with water to 100 ml. and filtered) are slowly added. The mixture is heated under a reflux condenser for 4 hours, and, after cooling, the liquid is diluted to 200 ml. with 2 per cent. (by vol.) sulphuric acid, and left in the dark for 24 hours. The precipitate is collected, and the flask and precipitate washed six times with 10 ml. of water, after which the precipitate is dried at 80° C. for one hour, cooled and weighed. One g. of 2-4.dinitrophenylhydrazone corresponds with 0·458 g. of camphor. With camphor itself the error was about 1 per cent. The synthetic hydrazone consists of golden-yellow needles of m.p. 164° C., and the natural hydrazone of orange needles melting at 174° C. With tincture of camphor the error rarely exceeded 3 per cent. All aldehydic and ketonic bodies present are included by this method, but their presence will be disclosed by the m.p. of the hydrazone. D. G. H.

Characteristic Reaction of Quinine Alkaloids. R. Monnet. (*J. Pharm. Chim.*, 1936, **128**, 454–459.)—Grahe's reaction consists in heating 25–30 cg. of the cinchona bark, either in pieces or pulverised, at first gently and then to red heat in a test-tube held vertically. White fumes are followed by a condensation of water-vapour on the cold sides of the tube, and subsequently red-violet fumes condense into carmine-red oily droplets, and a characteristic odour is emitted. This reaction has been studied in detail, but since certain quinine alkaloids as bases or salts do not give a direct reaction, the addition, before heating, of one drop of officinal lactic acid (or of citric or salicylic acid or lactose or potassium bisulphate), is recommended as a general practice. A yellow colour is then followed by a carmine-red. Under these conditions a positive reaction is given by quinine salts, esters, alkaloid preparations; by totaquina and all quinine drugs.
D. G. H.

Ionisable Iron in Foods. L. Shackleton and R. A. McCance. (*Biochem. J.*, 1936, **30**, 582–591.)—The ionisable iron in foodstuffs may be determined with $\alpha\alpha'$-dipyridyl. For flesh foods, the raw or cooked material is cut into small pieces with a stainless steel knife and thoroughly pulped in a mortar. Five portions (1 to 5 g.) are weighed into five tubes, A, B, C, D, and E, of 40-ml. capacity, graduated at 20 ml., and to all 10 ml. of sodium acetate-acetic acid buffer solution of pH 5·5 are added. Previously-cooked foods need not be heated, but raw foods are heated at this stage for 10 minutes at 100° C. After testing the pH of the

fluids in the tubes, 0·5 to 1·0 g. of sodium hydrosulphite is introduced into each tube. To tubes C and D 0·05 mg. of iron is added, and to A, B, C, and D, a few crystals of *aa'*-dipyridyl; E is retained as a blank. The contents of all the tubes are well mixed with a glass rod and allowed to stand overnight. Five ml. of absolute ethyl alcohol are then added, and the contents are again well mixed and allowed to stand for at least 8 hours, but generally overnight. The solutions are then made up to 20 ml. with distilled water and filtered through Whatman filter-papers No. 541. The amount of iron present is determined by matching the colour against a series of standards in a comparator. For the examination of fruits and vegetables, the material is prepared as before, and four portions are weighed out into the graduated tubes. To each tube 10 or 15 ml. of the buffer solution are added, and the tubes are heated in a water-bath for 10 minutes at 100° C. After cooling, the *p*H is checked, and 0·05 mg. of iron is added to two tubes and hydrosulphite to all. The volumes are then made up to 10 ml. with distilled water, and the contents of the tubes are well mixed and allowed to stand overnight. In the morning the contents are well stirred and filtered after an hour. Each filtrate is divided into two portions. To one, a few crystals of *aa'*-dipyridyl are added, and the colour is developed; the other serves as a blank. Standard iron solutions may be prepared by placing in twelve tubes of uniform bore, amounts of an iron solution such that 0·0025, 0·005, 0·01, . . . to 0·10 mg. of iron, respectively, are obtained. To each tube, 10 ml. of the buffer solution are added, then 0·5 to 1·0 g. of hydrosulphite, and 12 hours later, 5 ml. of absolute ethyl alcohol. Each solution is diluted to 20 ml. and the tube is sealed. This method was also used for the determination of total iron after ashing the material, but the use of thiolacetic acid is preferred. The ionisable iron was found to vary from 33 to 100 per cent. of the total iron according to the foodstuff, but was very constant for each type of material. It is suggested that the percentage of the total iron in the ionisable form is a more characteristic feature of any foodstuff than the total amount of iron. S. G. S.

Metallic Contamination of Foods. N. C. Datta. (*Proc. Indian Acad. Sci.*, 1935, **2**, 322–332.)—Aluminium vessels appear to be well suited for storage of water (*p*H 6·9) and for milk and milk products. Juices of fruits and vegetables in common use in India dissolve only small quantities of the metal under normal conditions of storage at ordinary temperatures; these quantities depend more on the nature of the organic acid present (and probably also on the buffering-capacity of the food) than on the titratable acidity. Tamarind water (which contains tartaric acid, *p*H 2·8 to 3·0) dissolves more than the other juices (up to 28·18 p.p.m. in 24 hours), and addition of salt increases this tendency, the total effect of the juice and salt being almost equal to the sum of their individual effects when acting separately. The amount of aluminium dissolved during the ordinary process of cooking is very small, but when acidic foodstuffs containing salt are cooked and stored for fairly long periods in aluminium vessels, the maximum quantity of aluminium added thereby to the daily (Indian) diet may be about 50 mg. Under such conditions corrosion starts at the air-liquid junction, pin-holes being formed, and its extent depends on the concentration of salt, the time of exposure, and the quality of the metal or alloy used. Food prepared in aluminium vessels

has no harmful effect on the rate of growth, reproduction or general well-being of rats. Aluminium was determined (after Bertrand and Levy, *Compt. rend.*, **1931, 192**, 525) by precipitating the phosphates of iron, aluminium and calcium by means of ammonium phosphate (in the presence of ammonium chloride and an excess of ammonia) from a hydrochloric acid extract of the ash of the material, silica being removed in the usual way. The calcium phosphate was dissolved in acetic acid at *p*H 4·2, and a solution of the residue in hydrochloric acid was treated with sodium thiosulphate (to reduce the iron), the aluminium being then reprecipitated with ammonium phosphate and ammonium acetate at the b.p.; it was then re-dissolved and precipitated, and finally collected by filtration, ignited and weighed. J. G.

Composition of Turkish Tobaccos. J. Vlădescu and N. Dimofte. (*Z. Unters. Lebensm.*, **1936, 71**, 358–360.)—The composition of a number of Turkish tobaccos is given, the results being expressed upon 100 g. of dry substance. The total nitrogen lies between the limits 1·6 and 3·7 per cent.:—Smyrna (lowest) 1·6 to 2·2, Erbaa 2·6 to 3·3, Brussa 2·7 to 3·2, Samsun 2·1 to 3·7, Edirne (highest) 2·5 to 3·7. The protein nitrogen lies between the limits 5·6 and 9·8 per cent.:—Smyrna 5·7 to 6·9, Erbaa 5·6 to 7·3, Edirne 6·9 to 8·9, Brussa 6·9 to 9·3, Samsun 6·5 to 9·8. The nicotine-content lies between the limits 0·7 and 3·6 per cent.: Smyrna (lowest) 1·1 to 1·3, Brussa 1·4 to 2·2, Samsun 0·7 to 2·8, Erbaa 2·5 to 3·0, Edirne (highest) 2·3 to 3·6. The total reducing power (Fehling), expressed as glucose, lies between the limits 2·5 and 18·5 per cent.: Smyrna (highest) 12·2 to 18·5, Brussa 7·7 to 13·7, Erbaa 7·3 to 12·3, Samsun 5·0 to 13·8, Edirne (lowest) 2·5 to 9·2. The soluble carbohydrate-content (expressed as glucose) lies between 1·1 and 15·9 per cent.: Smyrna (highest) 9·4 to 15·9, Erbaa 5·7 to 10·6, Brussa 4·5 to 10·3, Samsun 2·9 to 9·7, Edirne (lowest) 1·1 to 8·6. The ash varies from 12·0 to 23·5 per cent.: Smyrna 12·7 to 15·5, Edirne 18·0 to 23·5, Samsun 11·9 to 15·7, Brussa 12·4 to 17·7, Erbaa 13·5 to 15·5. Smyrna tobacco is thus characterised by a low content of nitrogenous substances (protein and nicotine), low mineral matter, high reducing power and high carbohydrate-content. Edirne–Adrianopole tobacco is characterised by high nitrogenous and mineral constituents, low reducing power and low carbohydrate-content. The authors state that Smyrna is a superior tobacco to Edirne. Tobaccos from the other sources lie between these in quality. By a comparison of the results found for different commercial grades of the same tobacco it is seen that the lower qualities have higher total nitrogen, protein and ash-contents, lower reducing power and lower carbohydrate-content. This is particularly noticeable in the grades of Smyrna tobacco. Figures are also given for the composition of tobaccos of the same commercial grade from fifteen different sources. A. O. J.

Biochemical

Modification of Young's Method for the Determination of Inositol in Animal Tissues. R. A. Gregory. (*Biochem. J.*, 1935, **29**, 2798–2802.)—For every 1 g. of tissue to be used, about 1 ml. of 10 per cent. potassium hydroxide solution is measured into a large pyrex boiling-tube, which is heated in a boiling water-bath, and the weighed amount of tissue is dropped in. The contents of the

tube are stirred occasionally with a glass rod, and heated for the minimum time to effect solution (usually 30 minutes), and the hot solution is washed into a 50-ml. flask, and neutralised with a solution of zinc chloride in hydrochloric acid ($ZnCl_2$ 126 g., concentrated hydrochloric acid 4·5 g. per l.). The strength of this solution is such that 1·5 ml. neutralises 1 ml. of 10 per cent. potassium hydroxide solution, and this should be checked by titration with alkali, with phenolphthalein as indicator. The required amount of the zinc solution is added to the hot solution in the flask with gentle agitation, a solid mass being formed. The flask is then heated in the water-bath for a few moments with gentle shaking. The precipitate becomes lighter and granular in character and the contents become fluid again. The flask is then cooled in a stream of cold water, and the contents are diluted to volume, and, after standing for a few moments, are filtered through a dry coarse paper. An aliquot portion (30 ml.) of the filtrate is transferred to a dry 250-ml. conical flask and 5 ml. of acid mercuric sulphate reagent (27 g. of mercuric sulphate dissolved in 100 ml. of 10 per cent. sulphuric acid w.w. at 5° C., and separated from any precipitate formed at room temperature) are added. The mixture is neutralised by the addition of solid barium carbonate until a drop of the solution does not redden blue litmus paper, the flask is stoppered and shaken for a short time, and the liquid is filtered through a dry Buchner funnel into a dry flask. The whole of the filtrate is poured into a dry 100-ml. beaker and saturated with hydrogen sulphide. After filtering through a dry paper into a dry flask, an aliquot portion of the filtrate is transferred to a 50-ml. beaker, evaporated on a water-bath to less than 5 ml., transferred to a 30-ml. centrifuge tube, and re-heated in the water-bath. To the hot solution, 2 g. of crushed crystalline barium hydroxide are added, the solution is heated for 5 minutes with occasional stirring, and the tube is then removed from the water-bath. Immediately 20 ml. of absolute ethyl alcohol are added slowly with vigorous stirring, the rod is removed, and the tube is allowed to stand, preferably in the ice-chest, for 2 to 3 hours, after which it is centrifuged at 3000 r.p.m. for 3 minutes, and the alcohol is poured off. The precipitate is stirred up in 10 ml. of hot water, the sides of the tube being well washed down at the same time, and then, from a graduated pipette, sufficient *N* sulphuric acid solution to acidify the solution is added, methyl red being used as an indicator. A small amount of Norit decolorising carbon is stirred into the solution, which is diluted to 25 ml. with hot water, the tube is heated in the water-bath for 45 minutes and then centrifuged at 3000 r.p.m. for 5 minutes, and the solution is transferred to a 100-ml. beaker. The precipitate is stirred with 20 ml. of hot water, re-heated for 30 minutes, and centrifuged, and the washing is added to the main solution. The solution is concentrated on the water-bath to 5 to 10 ml., then made up to 100 ml., and re-evaporated to 6 ml. or less. After cooling, 60 ml. of acetone and 30 ml. of ether are added slowly, the sides of the flask are scratched with a glass rod to induce crystallisation, and the flask is stoppered and placed in the cold room for 24 to 36 hours. The precipitate is collected on a sintered glass micro-filter (Schott and Gen., Jena, 12G3) or on asbestos in a small Gooch crucible, and well washed with acetone and finally with ether. It is dissolved in hot water, traces of ether being removed by heating the solution on the water-bath, and is then made up to 25 ml. in a volumetric flask. Five ml. of this solution (containing

not more than 1·0 mg. of inositol) are placed in a dry pyrex boiling-tube, and treated with 3 ml. of iodo-mercurate solution (288 g. of potassium iodide, dissolved in water, added to 108 g. of mercuric chloride in water with shaking, the solution being diluted to 1 litre) added from a 10-ml. micro-burette, 4 ml. of 30 per cent. sodium hydroxide solution and 2 ml. of a 20 per cent. barium sulphate suspension added from a wide-tipped pipette. After its contents have been mixed by gentle rotation, the tube, its mouth covered with a glass ball, is placed in a boiling water-bath for 30 minutes, and then removed (with as little disturbance of the contents as possible) to a bath of cold running water for 5 minutes. Eight ml. of 20 per cent. sulphuric acid are run slowly from a burette into the solution, and the whole is mixed by gentle rotation. After a further 5 minutes, 5 ml. of 0·02 *N* iodine solution are added from a standard pipette, and the contents of the tube are well mixed by rotation and by stirring with a glass rod which is left in the tube. After another 10 minutes, with occasional stirring, the solution is transferred to a 100-ml. beaker and the excess of iodine is titrated with 0·01 *N* thiosulphate solution from a 10-ml. micro-burette, starch solution being used as the indicator. A recovery of 90 per cent. of inositol, which was added to tissues, was obtained. S. G. S.

Action of Dyestuffs and other Substances on Milk Dehydrogenase. Identity of Schardinger Enzyme with Xanthine Oxidase. K. P. Basu and S. P. Mukherjee. (*J. Indian Chem. Soc.*, 1936, **13**, 11–18.)—The present work was carried out to determine the action of a series of dyestuffs, some narcotics, and other substances on the oxidation of xanthine and of aldehydes by milk dehydrogenase. It should be possible by this means to decide whether the Schardinger enzyme is identical with xanthine oxidase. The three substrates used were xanthine *M*/300, salicylaldehyde *M*/100 and acetaldehyde *M*/5, and the buffer was a *M*/3 phosphate buffer. The enzyme material was a 3 per cent. aqueous solution of the caseinogen preparation obtained by the method of Dixon and Thurlow (*Biochem., J.*, 1924, **8**, 976). Oxygen absorption measurements were carried out in Barcroft–Warburg respirometers at 37° C. Two ml. of the substrate, 4 ml. of the enzyme solution, and 2 ml. of the buffer were mixed and adjusted to various *p*H values, and the rate of oxygen absorption was measured. The optimum *p*H was found to be 8·0 for each substrate. It was found that at *p*H 8·0 with 4 ml. of enzyme solution in a total volume of 8 ml., the optimum substrate concentrations are:—xanthine, *M*/1200; salicylaldehyde, *M*/400; acetaldehyde, *M*/20. Under these optimum conditions the action of 26 dyestuffs was investigated by determining the amount of oxygen absorbed in certain periods by the enzyme, the substrate and the buffer, and also by the substrate, buffer and the enzyme which had already been subjected to the action of the dye for half-an-hour. The oxygen absorptions were compared and the inhibition caused by the dyestuff calculated. The results show that all the dyestuffs behave in exactly the same way towards xanthine and aldehyde oxidation by the milk enzyme. Only two of the acidic dyes investigated had any appreciable inhibiting effect on the rates of oxidation, and they had quantitatively the same inhibiting action in each of the three substrates. All the basic dyestuffs, with two exceptions, exerted a pronounced and equal inhibiting effect on the oxidation of xanthine and

of aldehydes. This action of all the dyestuffs makes it almost certain that in milk only one oxidising enzyme causes the oxidation of purine bases and aldehydes, and the active group in the enzyme appears to be acidic in nature. The investigation was extended to the effect of four narcotics and three other substances upon the rate of oxidation, the method adopted being similar to that used for the dyestuffs. The narcotics, diethylurea, ethyl urethane, phenylurethane and phenylurea had practically no effect on the oxidation either of xanthine or of the aldehydes. Of three other substances tested, pyrogallol had a pronounced but practically equal inhibitory effect upon both oxidations. Sodium hydrosulphite had practically no action, and gallic acid a slight inhibitory action upon both oxidations. All observations point to the identity of the Schardinger enzyme with xanthine oxidase.

A. O. J.

Contribution to the Methods of Determining Vitamin *A*. G. Balassa and G. Azanto. (*Hoppe-Seyler's Z. physiol. Chem.*, 1936, **240**, 29–32.)—A 0·02 per cent. aqueous solution of the dye "Parabraun Z extra" has been found suitable for comparison of the colour obtained with vitamin *A* concentrates by Rosenthal's reaction. The same colour was obtained by the addition of 3 ml. of antimony trichloride solution and warming, without the addition of guaiacol. These reactions give with cholesterol a red colour which, unlike the colour given by the vitamin, is unstable. The colour obtained with tissue extracts was bright red, but was too unstable for comparative measurements with the dyestuff. Rosenthal's reaction gives a colour having a diffuse absorption spectrum, with maxima at 545$m\mu$ and 478$m\mu$. S. G. S.

Absorption Spectrum of Vitamin B_1. F. F. Heyroth and J. R. Loofbourow. (*Biochem. J.*, 1936, **30**, 651–658.)—The variations in the ultra-violet absorption spectrum of vitamin B_1, previously reported by other workers, have been confirmed with specimens obtained from different sources. A correlation has been established between the biological activity and ultra-violet absorption, but owing to the ease with which the absorption is altered, this is regarded as a coincidence. The variations in the ultra-violet absorption spectrum may be due to the reversible dissociation of the vitamin into an aminopyrimidine derivative and a thiazole derivative, and also to the deamination of the aminopyrimidine. The curves given by Peters and Philpot (*Proc. Roy. Soc. Lond.*, 1933, **B113**, 48) for acid alcohol solutions most nearly represent the vitamin, whilst the curves of Holiday (*Biochem. J.*, 1935, **29**, 719) in neutral alcohol represent the breaking of the quaternary linkages of the thiazole ring, and other published curves represent intermediate stages accompanied by some deamination of the pyrimidine. The available evidence points to the pyrimidine component having one amino, one hydroxyl and two methyl (or one ethyl) groups as substituents; but the hydroxyl group is probably not in the 2-position. S. G. S.

Influence of Freezing upon the Antiscorbutic Activity of Potatoes. T. L. Isumrudowa. (*Z. Unters. Lebensm.*, 1936, **71**, 326–330.)—Potatoes preserved by freezing at relatively high temperatures tend to develop a sweet taste, owing to the cooling being insufficient to produce the conditions which restrict

respiration and the accompanying enzymic activity (*cf.* Zerewitinow, *Chem. u. Warenkunde der Früchte und Gemüse*, p. 550; Zilva *et al.*, *Exper. Work Vit. Lab. Inst. Plant*, p. 118; Morgan and Field, *J. Biol. Chem.*, 1929, **82**, 579; Abst., ANALYST, 1929, **54**, 483). The method of thawing has also an influence on the vitamin activity. Slow thawing, during which the water is absorbed by the cell membranes, results in only slight tissue changes; rapid thawing, on the other hand, results in the formation of considerable amounts of water, and the osmotic properties of the cells are impaired. It is thus essential to thaw the frozen material under conditions which prevent access of atmospheric oxygen and restrict the activity of oxidising enzymes. Experiments on animals (described in detail) showed that storage of potatoes at 2·5 to 3° C. is accompanied by a definite lowering in antiscorbutic value (*e.g.* to less than 166 antiscorbutic units per kg.), but if the potatoes are kept at temperatures not higher than −14° C. the antiscorbutic value will exceed 166 units per kg. If the thawing is carried out correctly the value may be higher than this. Potatoes immersed in hot water before cooking retain their antiscorbutic activity more completely than those immersed in cold water.

A. O. J.

Lactoflavin, a possible Contaminant of Vitamin-free Diets. G. C. Supplee, G. E. Flanigan, Z. M. Hanford, and S. Ansbacher. (*J. Biol. Chem.*, 1936, **113**, 787–792.)—Most commercial caseins and some "purified vitamin-free caseins" are contaminated with lactoflavin. This is not removed when dry commercial caseins are extracted with weak acetic acid and alcohol for long periods, for its presence is readily shown by examination in "black light" under proper conditions. Lactoflavin may be removed from casein by a six-step elution treatment with weak sodium chloride solution at the isoelectric point. The relative lactoflavin-contents of caseins and water-soluble vitamin concentrates have been found to be correlated with their growth-promoting properties. S. G. S.

Bacteriological

Preservation of Bacteria by Drying *in vacuo*. E. Leifson. (*Amer. J. Hyg.*, 1936, **23**, 231–236.)—After referring to the work of Otten and Brown and giving a summary of the former's review of earlier literature on the subject the author describes a convenient and efficient technique by means of which bacteria are dried *in vacuo* and thereby rendered capable of surviving for long periods. A drop of the suspension of bacteria, preferably in meat infusion, with an equal volume of blood, is placed on a number of small pieces of filter-paper or on perforated glass beads, 2 to 3 mm. in diameter, contained in small test-tubes (2 in. × ¼ in.) plugged with cotton-wool. These are put in a suitable rack, and the rack is placed in a museum jar with a glass cover which has been ground to fit and made to overlap the length of the jar by 1 inch. In the cover there is a small hole drilled, 6–7 mm. from one end, so that, by sliding the cover, the jar is closed or opened to the air through this hole. A glass nipple is ground to fit the upper side of the cover, and connection is thereby made with the air-pump. A layer of anhydrous calcium chloride or other dehydrating agent is also put in the

museum jar. The vacuum pump should reduce the pressure to 0·01 mm. of mercury. It is claimed that even such delicate micro-organisms as the meningococcus can be preserved in this manner for a long time—over 64 days according to one experiment—and the hardier bacteria, typhoid, dysentery, Brucella, coli, etc., when once dried have been found to live in dried air for twelve months. Short exposure to air for transference does not appear to damage even the more delicate micro-organisms. Variation undergone by the dried bacteria has still to be investigated. D. R. W.

Agricultural

Rapid Method for the Determination of Carotene, Xanthophyll and Chlorophyll in Artificially Dried Grass Meals. M. Pyke. (*J. Soc. Chem. Ind.*, 1936, **55**, 139–140T.)—One hundred mg. of grass meal are finely ground and shaken vigorously for 5 minutes in a centrifuge-tube with a mixture of 10 ml. of ether and 3 ml. of a 25 per cent. solution of potassium hydroxide in methyl alcohol (the solution should be quite clear). After centrifuging, the supernatant ethereal layer is drawn off, washed with water, and drawn into a 100-ml. Erlenmeyer flask through a sintered glass funnel containing anhydrous sodium sulphate. The methyl alcohol layer is poured off and washed once with ether, and the ether is washed with water, dried and added to the first ethereal solution. Extraction is then complete, and the combined ether solutions are evaporated, the pigments are dissolved in 25 ml. of petroleum spirit, and the solution is shaken with an equal volume of 85 per cent. aqueous methyl alcohol. The colours of the two layers are estimated by means of Lovibond yellow glasses. The upper layer contains the carotene, and the lower (methyl alcohol) layer the xanthophyll. The percentages are calculated from Ferguson's curve (ANALYST, 1935, **60**, 680). Chlorophyll pigments are estimated by extracting the grass meal twice more with 3-ml. portions of 25 per cent. potassium hydroxide in methyl alcohol, the combined yellow-green solutions are made up to 25 ml. and the colour is matched. Very woody grass meals may give a yellow-red rather than yellow-blue colour, and the strength of the blue component is a measure of the chlorophyll present. A reference curve is given, and the extremes show that 0·050 per cent. chlorophyll gives 23 yellow and 6·1 blue units, and 0·008 per cent. chlorophyll 2·1 yellow and 0·6 blue units. Results are given for 12 samples of grass meals from different sources. Carotene varied from 110 to 670 mg. per kg., xanthophyll from 0 to 490 mg. per kg., and chlorophyll from 0 to 7·2 per cent. D. G. H.

Thiocyanate Test for Soil Reaction. Modified Technique. L. W. Raymond. (*J. Soc. Chem. Ind.*, 1936, **55**, 138–139T.)—When using the thiocyanate test in the routine examination of a large number of soils, greater precision can be given by introducing a comparator and assigning numerical values to the red colours developed. The stock solution for the comparator is made by dissolving 15 g. of cobalt nitrate ($6H_2O$) in 10 ml. of a 0·075 per cent. solution of potassium chromate. Thirteen test-tubes are placed in alternate divisions of a rack and marked 0 to 12. Into tube 12 are run 15 ml. of the above solution, and into each of the other test-tubes 5 ml. of water. Ten ml. of solution are removed from

tube 12 to tube 11, and after mixing, 10 ml. are transferred to tube 10 and so on, until 10 ml. are removed from tube 1 and discarded, and in tube 0 there is water only. The tubes are corked and sealed, they are raised on blocks ½ in. above the base of the stand, a thin opal glass being placed at the back of the rack, and the front covered with a plate having a horizontal ½-in. slit or a series of round holes, ½ in. in diameter, through which the solutions are viewed. By means of a small marked test-tube approximately 2·5-g. portions of each soil sample are placed in numbered test-tubes, and to each tube 5 ml. of the alcoholic thiocyanate solution are added, the closed tubes being then placed in a shaker for 10 minutes, and left to settle. After 1 hour the colour is estimated, and again after 24 hours, when it has usually darkened somewhat. D. G. H.

Water

Colorimetric Determination of Nitrates in Water in the Presence of Chlorides. H. Caron and D. Raquet. (*J. Pharm. Chim.*, 1935, **128**, 446–447.)—In order to overcome the influence of chlorides in Grandval and Lajoux's colorimetric method for determining nitrates, the following procedure should be followed:—A known volume, *e.g.* 10 ml., of the water to be analysed is evaporated to dryness with 1 ml. of a 1 per cent. solution of sodium salicylate. The residue is cooled in a desiccator and treated rapidly with 1 ml. of pure sulphuric acid, and then, after thorough mixing, with 10 ml. of water and 10 ml. of ammonium hydroxide. The resulting colour is compared in a colorimeter with a standard solution of nitrate treated in the same way. D. G. H.

Organic

Copper Selenite as a Catalyst in the Kjeldahl Nitrogen Determination. E. J. Schwoegler, B. J. Babler and L. C. Hurd. (*J. Biol. Chem.*, 1936, **113**, 749–751.)—Copper selenite dihydrate is recommended as a catalyst in the Kjeldahl method of nitrogen determination. The time required to obtain a clear solution is considerably reduced, whilst the accuracy compares favourably with that obtained with other catalysts. The reagent is prepared by the method described by Hurd, Kemmerer and Meloche (*J. Amer. Chem. Soc.*, 1930, **52**, 3881). S. G. S.

Fatty Acids of Margosa Oil. R. Child and S. Ramenathan. (*J. Soc. Chem. Ind.*, 1936, **55**, 124–127T.)—The seed oil of *Azadirachta indica* is the neem oil of India and the margosa oil of Ceylon. As sold, the oil is frequently adulterated, particularly with coconut oil. The percentage of oil in 3 samples of seeds from different districts varied from 45·4 to 49 per cent. on the dry kernel. The characteristics of the oil from these and other samples (extracted with various solvents and expressed) were as follows:—sp.gr., 30°/30°; 0·9159–0·9182; n^{40}_{D}, 1·4616–1·4623; saponification value, 198·5–207·2 (a pressed oil); iodine value 69·3–75·2; thiocyanogen value, 54·3–57·3; Reichert–Meissl value, 1·7–3·8; Polenske value, 1·2–3·5; free fatty acids (oleic per cent.), 0·77–5·03; unsaponifiable matter, 0·7–1·1 per cent.; soluble acids per cent., 2·1–4·0; Hehner value, insoluble acids per cent., 90·4–93·3. The mixed acids were subjected to lead salt separation and

vacuum fractionation of the methyl esters according to the Hilditch technique, and the summarised data show 35·7 per cent. of "solid" acids and 64·3 per cent. of "liquid" acids made up of palmitic, 13·1; stearic, 18·5; arachidic, 2·3; oleic, 47·5; linolic acid, 15·3; unsaponifiable matter, 0·9; and undetermined 2·4 per cent. There is a molar ratio of saturated to unsaturated acids of approx. 1 : 1·8, and permanganate oxidation of the oil in acetone showed the presence of less than 1 per cent. of fully saturated glycerides. Calculating from a thiocyanogen value of 54·3 and iodine value of 71·5 and a content of 60 per cent. unsaturated acids, 41 per cent. (on the original oil) oleic acid was found (44·8 by fractionation analysis), and 18·3 of linolic acid (14·4 by fractionation analysis). D. G. H.

Elm-seed Oil. H. A. Schuette and C. M. Lunde. (*Oil and Soap*, 1936, **13**, 12–13.)—The seeds from the elm (*Ulmus americana*) have a waxy coating; their percentage composition was as follows:—Ash, 5·25 (soluble ash 2·97, insoluble ash 2·28); ethereal extract, 25·55; crude protein, 42·00; crude fibre, 4·40; and nitrogen-free extract, etc., 22·80 per cent. The oil is liquid at ordinary temperatures; green when extracted with petroleum spirit, and yellow when expressed. It had the following characteristics: sp.gr. at 20/20° C., 0·9288; n_D^{20}, 1·4554; coefficient of viscosity at 20° C. (centipoises), 0·3381; surface tension at 20° C. (dynes/cm.), 30·72; solidif. pt., 14·0° C.; saponification value, 273·0; iodine value (Wijs), 24·10; Reichert-Meissl value, 2·1; Polenske value, 33·9; thiocyanogen value, 16·18; hydroxyl number, 13·45; unsaponifiable matter, 1·0 per cent.; soluble acids per cent. (as butyric), 0·8; insoluble acids (Hehner value), 82·23; iodine value of fatty acids, 23·08; saponification value of fatty acids, 288·7. Methyl alcoholysis indicated approximately 50 per cent. of capric acid; and the calculated percentages of glycerol and total fatty acids (assuming the oil to be a mixture of triglycerides), were 14·9 and 92·8, respectively. The total fatty acids consisted of 82·82 per cent. of saturated acids, 8·83 of oleic and 8·36 per cent. of linolic acid. The characteristics of the oil fall within the limits recorded for European elm-seed oils, except for the Hehner value, which is higher. The oil, in its major aspects, appears to be the temperate-zone equivalent of the tropical coconut oil. D. G. H.

Inorganic

Phenylanthranilic Acid as an Oxidation-reduction Indicator. A. Kirssanow and W. Tscherkassow. (*Bull. Soc. Chim.*, 1936, **3**, 817–821.)—*o*-Phenylamino-benzoic acid (prepared from *o*-chlorobenzoic acid and aniline in presence of copper) is a serviceable oxidation-reduction indicator. The reagent is prepared from 1·07 g. of the acid dissolved in 20 ml. of 5 per cent. sodium carbonate solution and diluted to one l., 0·5 ml. being used in a titration. One drop of 0·1 *N* dichromate solution gives a pinkish-violet colour, which is discharged by ferrous salt. For the titration of ferrous salt the sulphuric acid concentration should be 0·6 *N*. W. R. S.

Separation of Tin Oxide from Various Oxides by Ignition with Ammonium Iodide. E. R. Caley and M. G. Burford. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 114–118.)—When mixed with a suitable excess of ammonium

iodide and heated at 425 to 475° C., stannic oxide is quantitatively converted to stannic iodide which volatilises completely. Tin oxide may thus be separated from oxides of iron, copper, lead and nickel, which form relatively non-volatile iodides, or from tungstic oxide and silica which remain unchanged; zinc oxide and antimony oxide, on the other hand, form volatile iodides, and are therefore not separable from tin oxide, but they can be removed in a similar manner to tin oxide. A correction for the impurities in ignited stannic oxide, such as is obtained by the nitric acid treatment of non-ferrous alloys, may be made in the following way:— The separated impure metastannic acid is ignited to constant weight in a porcelain crucible; it is then intimately mixed with about 15 times its weight of ammonium iodide. The crucible is heated in an electric furnace maintained at 425 to 475° C. until fumes have ceased to come from the crucible (about 15 minutes). After cooling, 2 to 3 ml. of conc. nitric acid are added, the acid is removed by evaporation, and the residual nitrates are converted into oxides by ignition at a dull red heat. The weight of oxides is deducted from that of the impure tin oxide. It is advisable to carry out a "blank" test for non-volatile matter in the ammonium iodide. In test experiments, ferric oxide, cupric oxide, lead monoxide, tungstic oxide, and silica mixed with varying proportions of tin oxide were recovered with errors amounting in general to only a fraction of a mg. Results in close agreement with certificate values were obtained with the use of the method for determining tin in Bureau of Standards samples of brass and bronze. S. G. C.

Determination of Small Quantities of Germanium. N. S. Poluektof. (*Z. anal. Chem.*, 1936, **105**, 23–26.)—The colorimetric method described utilises the blue colour produced by the reduction of germanomolybdic acid, $H_8Ge(Mo_2O_7)_6.28H_2O$. The reagent consists of 16 ml. of molybdate solution (equal volumes of 15 per cent. ammonium molybdate solution and strong nitric acid) diluted to 100 ml., 8 ml. of 5 per cent. ferrous ammonium sulphate solution, 40 ml. of saturated sodium acetate solution, and water to 200 ml. The acid chloride distillate containing the germanium must be treated with hydrogen sulphide at 3 to 4 *N* acidity, alongside a standard germanium solution (0·0001 g. per ml.) and a blank. The precipitates are left to settle for 24 hours, centrifuged, and dissolved in 0·1 ml. of 25 per cent. potassium hydroxide solution and 0·05 ml. of perhydrol; each solution is transferred to a 50-ml. cylinder, and treated with 1 ml. of 25 per cent. sodium sulphite solution, a few drops of dilute sulphuric acid, 25 ml. of reagent, and water to 50 ml. The solutions are compared in a colorimeter, the standard being matched first against the blank (correction for traces of silica and phosphoric acid). The above method is used for quantities smaller than 1 mg.; for larger quantities the author recommends Tschakirian's volumetric method, in which a neutralised sodium germanate solution is treated with glycerol or mannitol and titrated with alkali hydroxide (*Comptes rend.*, 1928, **187**, 229). W. R. S.

Colorimetric Determination of Rhenium by means of the Geilmann Reaction. L. C. Hurd and B. J. Babler. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 112–114.)—A study has been made of the Geilmann colorimetric method, which involves the formation of an intensely coloured compound said to be $ReO(CNS)_4$, by the interaction of potassium thiocyanate and stannous chloride with a

hydrochloric solution of a perrhenate. The best conditions are to treat 10 ml. of the perrhenate solution with 40 ml. of a solution containing 0·2 g. of potassium thiocyanate, 0·1 g. of stannous chloride, and sufficient hydrochloric acid to give a final acid concentration of 2 per cent. The mixture is kept for 7 minutes to allow the colour to develop fully; the coloured compound is then extracted by shaking with three successive portions of about 15 ml. of ether, butyl acetate or *cyclo*-hexanol. The colour of the combined extract is compared colorimetrically with that of the extract of a standard solution of rhenium which has been treated similarly. The colour does not remain stable for more than a few hours. The sensitiveness of the test is 0·5γ in 10 ml. S. G. C.

Detection of Rhenium by means of the Sodium Carbonate Bead. H. Yagoda. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 133–134.)—Rhenium can be distinguished from other elements by the formation of a transitory yellow colour in the sodium carbonate bead. The reaction is observable with 0·015 mg. of rhenium when the bead is heated either in the oxidising or reducing flame. The test can be applied in the presence of small quantities of manganese by heating the bead in the reducing flame. S. G. C.

Determination of Small Amounts of Potassium by means of Silver Cobaltinitrite. R. J. Robinson and G. L. Putnam. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 211–213.)—Potassium is precipitated by means of silver cobaltinitrite, and the nitrite in the precipitate is determined colorimetrically by means of the Griess reagent; the method is a modification of existing processes on these lines, which are critically reviewed. The silver cobaltinitrite reagent is prepared by dissolving 25 g. of sodium cobaltinitrite in 150 ml. of water containing 50 g. of sodium nitrite, and adding, with stirring, 5 ml. of water containing 2 g. of silver nitrate; it is kept at 4 to 6° C. and centrifuged before use. *Method.*—To 1 ml. of the potassium solution, contained in a 15-ml. centrifuge tube, 1 ml. of reagent is added. After 2 to 3 hours at 0° C. the liquid is centrifuged at 3000 r.p.m. for 15 minutes. The supernatant liquid and the liquids subsequently used for washing are removed by syphoning. The precipitate is washed successively by centrifuging for 5 minutes with well-cooled liquids as follows: 5 ml. of water, 5 ml. of a 60 per cent. solution of acetone in water, and finally several 5-ml. portions of 99·5 per cent. acetone. The precipitate is dissolved in 1 ml. of 0·1 *N* sodium hydroxide solution by heating the tube in boiling water for 10 to 15 minutes. The solution is diluted to approximately 50 ml. in a Nessler glass, acidified to give a 10 per cent. strength of acetic acid, and treated with 2 ml. of sulphanilic acid solution mixed with 1 ml. of α-naphthylamine solution (strength not stated; reference: *Amer. Public Health Assoc.*, "Standard Methods for the Examination of Water and Sewage," 1933, 7th Ed., pp. 19–20). The colour developed is compared in a colorimeter of the Duboscq type with a standard solution of a similar small quantity of potassium salt which has been treated throughout in the same manner. Good results are cited of tests on pure solutions and a hard water containing 0·005 to 0·1 mg. of potassium per ml. A minimum of 0·050 mg. of potassium per ml. could be detected by precipitation at room temperature, and 0·002 g. per ml. by precipitation at 0° C. S. G. C.

Colorimetric Determination of Peroxides in Unsaturated Compounds. **C. A. Young, R. R. Vogt and J. A. Nieuwland.** (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 198–199.)—The method depends on the formation of ferric thiocyanate when the peroxide reacts with a solution of ferrous sulphate and ammonium thiocyanate. The reagent is prepared by dissolving 5 g. of ammonium thiocyanate and 5 ml. of 6 *N* sulphuric acid in 1000 ml. of absolute methyl alcohol, and saturating this with ferrous ammonium sulphate. The faint pink colour of the reagent is evaluated by colorimetric comparison with a colour standard, and the value is deducted from that obtained in the subsequent determination of peroxide. The colour does not darken appreciably in 1 hour, and the reagent may be preserved in an inert atmosphere for long periods. Colour standards, which should be freshly prepared each day, as they tend to fade, are made by adding ammonium thiocyanate and sulphuric acid, in the same proportions as used in the reagent, to a standard solution of ferric chloride in absolute methyl alcohol. A colorimeter of the Duboscq type is recommended. To determine peroxide, sufficient of the compound in methyl alcoholic solution is added to a 10-ml. portion of the reagent to yield a colour equivalent to that of 0·00002 to 0·0002 mol. of ferric thiocyanate per l. With many peroxides, such as are present in butyl-acetylene or 1-hexene, the colour develops fully in a few seconds, and is without delay compared with a standard of similar depth of colour. Some other peroxides, *e.g.* that found in diamylene, react more slowly, and it may be necessary to heat the liquid nearly to boiling for 4 to 5 minutes to accelerate the reaction. One mol. of peroxide reacts with two equivalents of ferrous sulphate. Quantitative results were obtained in tests with hydrogen peroxide and pure succinyl peroxide. It is pointed out that the method may not be applicable to some peroxides, such as benzoyl peroxide, which reacts extremely slowly, if at all, with ferrous sulphate. Marks and Morrell's potassium iodide method (ANALYST, 1929, **54**, 503), which is effective for such peroxides, is, however, liable to error in the presence of unsaturated compounds, owing to addition of iodine to the unsaturated linkage. S. G. C.

Detection and Determination of Hydrobromic Acid in Hydrochloric Acid. L. Chelle. (*Ann. Falsif.*, 1936, **29**, 229–231.)—To detect hydrobromic acid in the presence of a large amount of hydrochloric acid, 8 drops of pure hydrochloric acid, 8 drops of 10 per cent. potassium chromate solution, and 2 ml. of pure sulphuric acid are added to 10 ml. of a solution containing bromide or hydrobromic acid in a test-tube, and mixed by shaking. After the mixture has been kept for 5 minutes in cold water, 2 ml. of sulpho-fuchsine reagent (*cf.* Denigès et Chelle, *Bull. Soc. pharm. Bordeaux*, 1912; C.R., 1912, p. 1010; ANALYST, 1913, **38**, 119) and 2 ml. of chloroform (preferably washed with water to remove all trace of alcohol) are added. The mixture is shaken for at least 1 minute. On standing, the chloroform becomes violet, the depth of colour depending on the amount of bromine present. Unlike the iodine colour, this does not disappear on addition of sodium thiosulphate. The presence of 0·005 mg. of bromine may be detected.

In applying this method to the determination of the bromine-content of wines (*cf.* ANALYST, 1936, 343), abnormally intense colours were obtained in some instances, and these were traced to the presence of hydrobromic acid in the hydrochloric

acid used. Two stocks of hydrochloric acid, *A* and *B*, sold as pure, behaved in this way, and even produced very pronounced colours in blank tests on distilled water; a third stock of acid, *C*, was satisfactory. The acids *A* and *B* also produced a deep pink colour in the preparation of the hydrostrychnic reagent of Denigès (*Précis de Chim. anal.*, I, p. 69) used for determining nitrites in waters.* The test described above was used to determine the bromine-contents of the acids *A* and *B*, for which purpose these acids were diluted 20-, 40-, 60- and 80-fold with distilled water, and the colours obtained were compared with those obtained with potassium bromide solutions containing 0·25 to 10 mg. of bromine per litre. The results varied, according to the dilution of the acids, from 108 to 130 mg. of bromine per litre of the concentrated acids. E. B. D.

Direct Titration of Sulphate. R. T. Sheen and H. L. Kahler. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 127–130.)—Schroeder's method (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 443), in which tetrahydroxyquinone is employed as internal indicator, has been studied. The following modified procedure was devised with special reference to the testing of boiler-feed water, and to render the method applicable to larger amounts of sulphate. The sodium tetrahydroxyquinone indicator is not stable in solution, and it is therefore used in the form of an intimate mixture with 300 parts of potassium chloride, prepared by grinding the dry materials together sufficiently finely to pass a 100-mesh sieve. *Method.*—A 25-ml. portion of the solution is rendered just acid to phenolphthalein, and 25 ml. of alcohol (ethyl or *iso*propyl) are added. The dry indicator mixture is added (see Table below) and dissolved by shaking, and the solution is titrated with standard barium chloride solution until the yellow colour changes to rose-colour; strong illumination is necessary to detect the end-point. With amounts of sulphate greater than 2000 p.p.m., sodium chloride must be added to the solution in accordance with the following table:

Sulphate ion concentration p.p.m.	Quantity of indicator g.	Strength of standard barium chloride solution[1]	Sodium chloride crystals required g.
Up to 100[2]	0·1	1	—
100– 1,000[2]	0·2	1	—
1,000– 2,000	0·2	4	—
2,000– 4,000	0·4	10	2
4,000–10,000	0·4	10	4
10,000–20,000	0·6	50	8
20,000–30,000	0·8	50	8

[1] Number of mg. of SO_4 to which 1 ml. is equivalent; the solution is standardised gravimetrically.

[2] 0·1 ml. of barium chloride solution to be deducted as "blank."

With phosphate ion present in amount up to 60 p.p.m. (the maximum allowable) the solution should be rendered just acid to bromocresol green (*p*H 4). More than 5 p.p.m. of iron or aluminium should not be present. The amounts of other ions which can be tolerated depend on the amount of sulphate present; not more than the following may in general be present: 1500 p.p.m. of silicate, 1400 p.p.m. of magnesium, 300 p.p.m. of calcium, and 80 p.p.m. of tannin. S. G. C.

* This reagent is prepared by heating 5 ml. of a 1 per cent. solution of strychnine with 5 ml. of pure hydrochloric acid (sp.gr. 1·18) and 3 to 4 g. of pure granulated zinc to boiling-point and allowing the test-tube to stand for 5 to 10 minutes.

Determination of Selenium in Steel. W. C. Coleman and C. R. McCrosky. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 196–197.)—The apparatus, to which the required quantities of solutions are added as indicated, is shown in Fig. 1. A 5-g. sample of the steel is placed in flask *A*. The ground stopper is inserted and the steel is dissolved by gentle heating. The solution is finally boiled and evaporated to a volume of 25 to 30 ml. The contents of flask *A* are transferred to flask *B*, the liquid is digested on a hot-plate for 15 minutes, and the residue, together with the macerated paper, is filtered off on a Gooch crucible with a filter-paper bed. The precipitate of selenium, which is contaminated with a little iron, etc., is washed with water and transferred back to flask *B*, and sufficient of a 1 per cent. solution of bromine in hydrochloric acid (about 5 ml.) is added to dissolve the residue and yield a yellow solution. The liquid is heated under a reflux condenser for 5 minutes, 50 ml. of water containing 1 ml. of a saturated solution of acetanilide in alcohol are then poured down the condenser tube, to destroy any bromine not removed in the refluxing process. The condenser is removed, and 20 ml. of 2·5 per cent. sodium fluoride solution are added to suppress the interference of ferric ion; the solution is cooled to 20° C. and diluted to 150 ml., and the selenious acid is titrated by the use of 0·02 *N* solutions of iodine and thiosulphate, with starch as indicator, according to the Norris and Fay method (*Amer. Chem. J.*, 1896, **18**, 703; ANALYST, 1897, **22**, 82). The method gave results in close agreement with those furnished by a gravimetric method in which the selenium was separated from the steel by distillation as tetrabromide, which was subsequently reduced to elementary selenium and weighed. S. G. C.

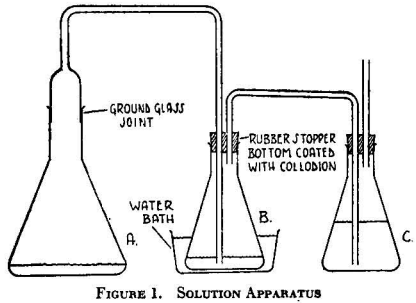


FIGURE 1. SOLUTION APPARATUS

A. 500-ml. Erlenmeyer flask containing 50 ml. of 1.18 hydrochloric acid and 1 ml. of 0.1 *N* iodine in potassium iodide
B. 250-ml. Erlenmeyer flask containing one-fourth filter paper (Whatman No. 40, 9 cm.) finely macerated, and 5 ml. of 0.1 *N* iodine in potassium iodide diluted to 100 ml.
250-ml. Erlenmeyer flask containing 200 ml. of water.

Ignition of Silicic Acid. K. A. Krieger and H. S. Lukens. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 118).—Heating a moist silica precipitate together with the damp filter-paper in a covered platinum crucible over a large Méker burner resulted in the formation of an appreciable amount of a black substance which was very resistant to oxidation. It was identified as silicon carbide, the formation of which is noteworthy, in view of the fact that the temperature of heating was not higher than 930° to 950° C. S. G. C.

Microchemical

Vitali's Reaction. New Technique for its use as a Quantitative Micromethod. C. Morin. (*J. Pharm. Chim.*, 1936, **128**, 545–547.)—The dry residue obtained in Vitali's reaction after evaporation with fuming nitric acid is dissolved in about 10 ml. of anhydrous acetone, and a 10 per cent. alcoholic solution of potassium hydroxide in methyl alcohol is added, drop by drop. Atropine and

hyoscyamine in particular give violet colours more intense and more stable than the fugitive striations obtained by the usual procedure. For a sample of 0·5 to 0·1 mg. the colour is stable for ten to fifteen minutes. For micro-estimations the acetone solution is washed into a colorimeter cell graduated from 5 to 10 ml., and the type solution is placed in another similar cell. The potassium hydroxide solution is added to each, drop by drop, until no further deepening of colour occurs, the solutions both made up to the mark with acetone, and the colours read. An intense violet is given by 0·5 mg. of atropine and 5 ml. of acetone, a dark lilac with 0·04 mg., and a dark rose-colour with 0·01 mg. D. G. H.

Micro-distillation Apparatus. L. M. Craig. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 219–220.)—An apparatus permitting the distillation of up to 0·2 ml. of liquid is shown in Fig. 1. The main part is made from glass tubing approximately 17 mm. in diameter. The lower part is drawn out to a capillary (30 mm. long; inside diameter 1 mm.) ending in a thin-walled bulb, *A*, of 0·25-ml. capacity, into which is put the material to be distilled. Inside the capillary, and almost filling it, is an ebullition stick formed of a glass rod, *B*, having sealed on to its lower end a 1-mm. length of capillary tubing. The condenser, *C*, is provided with a ground-in joint at *F*, and its top is closed by a rubber stopper carrying a water-inlet

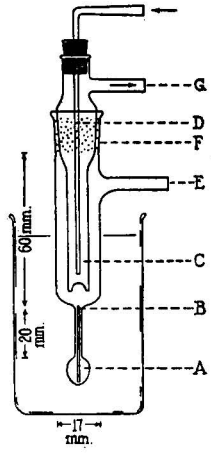


Fig. 1

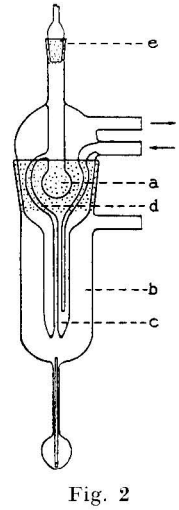


Fig. 2

tube, *D*, which extends nearly to the bottom of the condenser. During distillation, liquid condenses on the tip of *C*, where it is held by surface attraction; the concavity permits up to 0·2 ml. to collect. The distillate is removed from the condenser by means of a capillary pipette, the last traces being recovered by means of a solvent. Heating is carried out by means of an oil bath provided with a mechanical stirrer and a thermometer. When the volume of distillate is more than 0·2 ml., the use of a modified apparatus (Fig. 2) is proposed. The condenser has sealed into it a capillary tube, *d*, leading up from the bottom to a collecting bulb, *a*. During distillation the liquid collecting at *c* is caused to pass up into the bulb at *a* by reducing the air-pressure slightly at *e*. S. G. C.

Micro-determination of Copper. F. Hecht and R. Reissner. (*Mikrochem.*, 1935, **17**, 127–134.)—Three methods employing the Emich filter-stick procedure have been tested:—(*a*) precipitation with 5·7-dibrom 8-hydroxyquinoline, (*b*) precipitation as copper benzoinoxime, (*c*) precipitation as copper salicylaldoxime. All the methods give good results, but the first is recommended, as the oxime has the lowest copper percentage (9·53). The method used is adapted from that of Berg (*Mikrochem. Emich-Festschrift*, 1930, p. 26). The test solution is evaporated to dryness in a porcelain crucible or a micro-beaker and taken up in 0·1 to 0·2 ml. of dilute (1 : 10) nitric acid and a few tenths of a ml. of hot water; it is sucked into a micro-beaker (Jena glass bottle-shaped beaker with sintered glass filter attached) and washed until the final volume is 2 ml. or less. Then 0·1 ml. of acetone is added, and the micro-beaker is warmed to 50° C. A saturated acetone solution of dibromoxine (about 0·3 per cent.) is added, drop by drop. Every 0·1 mg. of CuO requires about 1 ml. of reagent to give the usual 3 to 4 times excess. After 10 minutes on a gently boiling water-bath the mixture is filtered warm, and the precipitate is washed three times with wash liquid (0·4 ml. of 6·5 per cent. nitric acid, and 15 ml. of acetone diluted to 20 ml. with water), and dried for an hour at 110°–115° C. The method is suitable for amounts up to 1 mg. of CuO. When a crucible and porcelain filter-stick are used instead of the filter-beaker the acetone tends to cause creeping. J. W. M.

Physical Methods, Apparatus, etc.

Enumeration of Microscopic Objects. A. C. Fay. (*J. Lab. Clin. Med.*, 1935, **20**, 1088–1089.)—The specimen (0·1 ml. or 0·1 g., diluted quantitatively if necessary) is spread over the entire area of a clean glass slide (3 × 1 in.) with the aid of water, and dried, fixed and stained as required. With the aid of a stage micrometer and with a given objective and a given ocular in use, the tube length of the microscope is so adjusted (and recorded for subsequent occasions) that the area of the field bears a convenient ratio to the total area of the slide, *e.g.* 1 : 1000, or 1 : 100,000. By making counts on a number of fields at different parts of the slide, and multiplying the average number of objects per field by the appropriate ratio, the total number of objects on the slide is obtained. If a suitably ruled disc is inserted in the ocular, measurements and countings can be limited to a central part of the field where the definition is best. (*Cf. J. Dairy Sci.*, 1933, **16**, 311.) J. G.

Inorganic Liquid Mixture for a Heating Bath. B. E. Christensen and A. E. King. (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 194.)—A mixture of 1 to 6 parts of orthophosphoric acid (85 per cent.) with 1 part of metaphosphoric acid has been found advantageous for use, instead of oil, fusible metal or sulphuric acid, for a heating bath for temperatures from 100° to 250° C. Before use the mixture is slowly heated to 260° C. and kept at that temperature until steam ceases to be given off. Fumes are not evolved below 340° C. Mixtures with the lower proportions of orthophosphoric acid are solid or viscous at room temperature, but those with the higher proportions are mobile. A bath with 3 parts of orthophosphoric acid to 1 part of metaphosphoric acid has been used for over a month with no apparent change in properties. S. G. C.

Reviews

COLLECTED SCIENTIFIC PAPERS OF SIR WILLIAM BATE HARDY, F.R.S. Pp. xi+932. Cambridge University Press. 1936. Price 63s. net.

Professor Rideal and the Cambridge Press have done signal service both to pure and applied science in giving us this excellently produced volume of Hardy's papers. It is a record of the thought and work of a great man and a noble character, one who loved life and loved to study its manifestations; who pursued science with energy rarely equalled, absolutely without taint of self-seeking; and whose interests and pioneering discoveries covered so many different aspects of nature that any attempt to classify his work under the modern professional subdivisions of natural science is futile. There is a rare distinction and greatness in this collection.

The papers cover the period from 1891 to 1934. There are, first, some thirteen papers on zoological subjects, mainly, but not exclusively, investigating wandering cells charged with the duty of protecting the organism from dangerous invaders. Then in one year (1899) come two papers of epoch-making importance. The first, on "The Structure of Cell Protoplasm," proved that most of the curious structures observed, and disputed over, by histologists have nothing to do with the living cell and its activities, being artificially produced by precipitation of the colloids present in the protoplasm when the cell dies or is "fixed" for microscopic observation by the powerful reagents generally employed. The second laid the foundation of the modern knowledge of colloidal electrolytes by showing that proteins migrate in an electric field—to the cathode if the solution is acid, to the anode if it is alkaline —becoming coagulated on reaching the electrode to which they migrate. The existence of the "*iso*electric point" was here established for the first time. There follow several more papers on colloids, including the classical ones on the globulins. From 1908 to 1913 we find Hardy going yet deeper into the mechanism of his beloved colloids and living systems, laying one of the foundations of modern surface chemistry in the paper (No. 32), where the idea of special orientation of molecules under the influence of chemical forces at interfaces is advanced for the first time. He is fully convinced that knowledge of surface action will illuminate the behaviour of living cells, since surfaces form so large a part of their structure. There is a hint of his energy in one or two mathematical papers; about this period Hardy determined to acquire advanced mathematical technique, which had not been included in his early training as a zoologist and physiologist. Just after the war the very important researches on friction and lubrication were commenced; the first of these alone (No. 37) will repay reading and re-reading at this time by anyone interested in the nature of friction, and the whole series of over a dozen papers forms a most important contribution to the science of lubrication. Not only lubrication, but also the cold storage of food, claimed Hardy's attention among the practical problems of industry; there are a few papers on the freezing of colloidal systems, hinting at, but not revealing the magnitude of, his work as Director of the Low Temperature Research Station in Cambridge.

At intervals throughout the volume there are essays on the major problems of biology; particularly on the possibility of explaining, ultimately, in terms of known

properties of molecules and the forces about them, the way in which one part of a living cell controls all the occurrences within the cell boundaries, and also transmits the power of reproducing the form and the characteristic activities of the cell to innumerable generations of daughter cells. No one knew better than Hardy how far we still are from such a goal, and no one did more to advance science towards this goal. He lived and worked mostly in the School of Physiology in Cambridge—a school in which science flourished, as a whole and in very many branches, in a way never to be forgotten by one who had the privilege of working there. Perhaps the most vigorous period of this school was before its subdivision, after the war, into separate departments of Biochemistry and Physiology, when numerous future winners of Nobel prizes worked, sometimes in cellars or behind green baize curtains, under crowded conditions which, in spite of discomforts, had some advantages in the way of interchange of scientific ideas over the modern, more sumptuously equipped, and better partitioned institutions. May science never become so irrevocably subdivided that it can no longer breed men like Hardy!

N. K. ADAM

PHYSICAL ASPECTS OF ORGANIC CHEMISTRY. By WILLIAM A. WATERS, M.A., Ph.D. With an Introduction by Professor T. M. LOWRY, C.B.E., D.Sc., F.R.S. Pp. xv+501. London: George Routledge & Sons, Ltd. Price 25s.

The most striking change in organic chemistry in recent years has been the increasing importance of physical methods and physical theories. Not only is it common at the present time to find problems investigated from the standpoint of reaction velocity, dissociation constant or dipole moment, but an organic chemist rarely regards his work as complete unless he can offer some kind of interpretation in terms of the electronic theory of valency. Those who learnt their chemistry fifteen or more years ago find difficulty in following the arguments involved, and the student of to-day has so much material before him that he is apt to be bewildered by it. Chemists, therefore, owe a debt of gratitude to Dr. Waters for his book on the "Physical Aspects of Organic Chemistry," which takes the reader by stages from the dualistic theory of Berzelius to the modern electronic theories of aromatic substitution and reactivity.

The chapter headings will give some indication of the scope of the book. Chemical Affinity; Physical Theories of Molecular Structure; Valency; Electrical Dipoles; Chemical Reactivity; Unsaturation; Free Radicals and their Non-ionic Reactions; Ionisation and Ionic Reactions; Acidity; The Reactivity of Halogen Compounds; General Polarity; Hydrolysis and Esterification; Ionotropic Change; Molecular Rearrangement; Conjugation; and Aromatic Compounds, (*a*) Aromatic Structure and (*b*) Theories of Aromatic Substitution. The subjects discussed are by no means free from controversy, but the author has tried to "survey a wide range of chemical theories rather than to devote particular attention to a few specialised theories. The historical aspect of a rapidly developing subject has been kept continually in view, with the intention of giving a general outline of theoretical organic chemistry rather than one *ad hoc* point of view."

Dr. Waters has written an original work in an able manner. Very little previous knowledge of the topics considered is pre-supposed, and there are

frequent references to the literature of organic and physical chemistry; these matters will be appreciated by the reader whether he is new to the subject or already has some acquaintance with it. The book can be warmly recommended; it covers an aspect of organic chemistry which does not appear to be dealt with so completely in any other book, and the author is to be congratulated not only on his courage in attempting a difficult task, but also on the success with which it has been accomplished.

S. GLASSTONE

SULFURIC ACID MANUFACTURE. ANDREW M. FAIRLIE. American Chemical Society Monograph Series. Pp. 669. New York: Reinhold Publishing Corporation; London: Chapman & Hall, Ltd. Price 48s. 6d.

Sulphuric acid is still the most important of the heavy chemicals, and the appearance of an authoritative work on the subject is a matter of some moment. The author has a considerable reputation in the United States, and has had the benefit of advice and information from both American and European sources.

The principal and only really serious criticism the British reader will make is that spent oxide and hydrogen sulphide as sources of sulphur are treated in an inadequate and rather cavalier fashion; the former is dismissed in a dozen lines and the latter in three. The statement that in England spent oxide "is burned in furnaces similar to those used for pyrites fines" is not entirely accurate. Much spent oxide is burned either in hand kilns or mechanical furnaces different from the fines burners described.

After a general introduction and a survey of production and construction materials the author deals with burners, roasters and furnaces and the cleaning, and so on, of the resulting gases. Apart from the—to a British reader—irritating omissions noted above, the ground is well covered, and there are sections dealing with flash roasting and the utilisation of converter and blast furnace gases. The subsequent 140 pages are devoted to chamber processes—correctly termed by the author "nitration processes." The classical process and modern modifications, *e.g.* Mills–Packard, Gaillard–Parrish, Petersen, Schmiedel and other processes, are well treated. The minutiae of details of construction, control and operation depend largely on local circumstances and on the views of the individual manager, and the author may receive occasional minor criticisms of varying degrees of justification relative to his treatment of these. Purification, which the author rightly considers to commence with choice of good raw materials and efficient cleaning of burner gases, and concentration of acid are next dealt with.

More than 200 pages are devoted to a comprehensive survey of the available knowledge relating to the contact process. The platinum *versus* vanadium question is reviewed impartially, and an account is given of the legal and polemical controversies regarding the preparation of vanadium catalysts. The chapter on special types of contact plant and individual installations is particularly good. The combination of cement and acid manufacture, as practised both in this country and on the Continent, which is casually mentioned in the text, might also have been dealt with here.

The final chapter is devoted to miscellaneous matters, mixing and shipping, hazards and safety measures, costing, to buy or to build (a very good section),

choice of process and trends in the industry. With regard to the last-mentioned subject, the author is probably correct in his opinion that the potentialities in the newer nitration processes may be of far-reaching importance. The classical lead chamber process is held to be obsolescent in the United States. This view is not universally held in this country. The book concludes with a number of very useful tables.

The author has produced a very useful book, and for the American reader for whom it is, presumably, primarily intended, an eminently satisfactory one. An additional 10 or 20 pages devoted mainly to spent oxide and hydrogen sulphide and their burning would have made it equally complete for readers in this country. In fairness it should be said, however, that where American and European practice coincide, the author has not hesitated to go outside the United States for the most up-to-date information. A pleasing and useful feature is the description with photographs, plans and operative details of actual plants. The book is well produced, and there are many references to the literature. J. S. CARTER

A SYNOPSIS OF THE BRITISH PHARMACOPOEIA, 1932, AND OF THE POISON LAW. By H. WIPPELL GADD. Thirteenth edition. Pp. 200. London: Baillière, Tindall & Cox. Price 3s.

This little book, of pocket-book size, has become a constant companion and reference work for many classes of workers besides the pharmacists for whom it was originally written.

The latest edition will be of particular service to analysts, because it includes a summary of, and guide to, the Poisons List and Rules, which became effective in May of this year.

As in previous editions, the book contains in tabular arrangement the whole of the drugs and preparations which are "official" in the Pharmacopoeia, together with strengths and doses. As an *aide-mémoire*, it is the most useful book of its kind printed in our language.

Several small errors and inconsistencies will be noticeable to critical readers, but doubtless the author will correct these in any reprint, and in the meantime, the little book will continue to serve a very useful purpose.

C. EDWARD SAGE