

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 2nd, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of:—Alfred George Avent, A.I.C., William Rhys Davies, F.I.C., Ernest Roadley Dovey, A.R.C.Sc., F.I.C., James Gray, F.I.C., James Henderson, B.Sc., A.I.C., Claude Alexander Scarlett, B.Sc., A.K.C., A.I.C., Percy Arthur William Self, B.Sc., F.I.C., Thomas Brooks Smith, B.Sc., A.R.C.S.

Certificates were read for the second time in favour of:—John William Haigh Johnson, M.Sc., F.I.C., Mamie Olliver, B.Sc., A.I.C., and George Edward Shaw, B.Sc.

The following were elected Members of the Society:—Alfred Norman Leather, B.Sc., F.I.C., Richard Harold Morgan, B.Sc., A.I.C., and William George Painton, B.Sc., A.I.C.

The following papers were read and discussed:—"Chemical Tests in Relation to Fur Dermatitis," by H. E. Cox, M.Sc., Ph.D., F.I.C.; "A Nomogram for use in Gas Analysis," by J. H. Coste, F.I.C.; "The Composition of Irish Winter Butter," by P. S. Arup, A.C.G.I., M.Sc., F.I.C.; and "Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates: XVI. Observations on Tartaric Hydrolysis; XVII. The Quantitative Precipitation of the Earth Acids and certain other Oxides from Tartrate Solution," by W. R. Schoeller, Ph.D., and H. W. Webb.

NORTH OF ENGLAND SECTION.

A MEETING of the Section was held at Manchester on October 19th. The Chairman (Mr. S. E. Melling) presided, and there were present the President (Mr. E. Hinks) and 28 Members.

Messrs. H. M. Mason, M.Sc., F.I.C., and A. R. Tankard, F.I.C., opened a discussion on "Quality in Relation to Foodstuffs." A most interesting debate followed, in which the following took part:—The President, Prof. W. H. Roberts, Messrs. J. Evans, E. M. Hawkins, C. J. H. Stock, G. D. Elsdon, and J. Hanley. A communication on the subject was read from Dr. J. T. Dunn.

Meniscus Corrections involved in the Calibration of Graduated Tubes.

By A. MORE, F.I.C.

It is impossible to conduct the calibration of some forms of apparatus used in gas analysis, such as closed tubes, in the position in which they are used. The usual method employed is to determine the volume of water or mercury required to fill the tubes in the inverted position until the horizontal plane tangential to the meniscus corresponds with the graduated marks, and then to deduct, when water is used, or add, when mercury is used, the so-called "meniscus error" to compensate for the reversed direction of the meniscus curve with reference to the graduation marks in the two positions. When the same liquid is used in the calibration of, and in the measurements with, gas vessels, the meniscus error is double the meniscus correction, which is the volume in the tube between the horizontal plane tangential to the meniscus and the surface of the water or mercury, as the case may be.

A similar problem arises in the calibration of small tubes designed to measure the volume of insoluble or extraneous matter collected by sedimentation or centrifugal separation from certain liquid media. The deposits obtained by sedimentation have, and those obtained on centrifuging can (with suitable manipulation) be arranged to have a horizontal upper surface. The tubes can be calibrated conveniently by weighing them empty and with liquids adjusted to the graduated marks, but, in this case, the difference between the volumes of the sediment and of the liquid filled to the same mark amounts to a single meniscus correction.

It is found, however, that the values of the double meniscus correction, given in different text-books dealing with the calibration of gas burettes for both water and mercury, differ materially. Treadwell and Hall's *Quantitative Analysis* (1928, p. 639) gives one series of values, supplied by W. Schloesser, and *Sutton's Volumetric Analysis* (1924, p. 519) gives another, the former agreeing with values given in Kurt Arndt, *Handbuch der Physikalisch-Chemischen Technik*, and the

latter with the values obtained by H. Göckel, quoted in Landolt and Börnstein's *Physikalisch-Chemische Tabellen*, 3rd edn., p. 29.

Göckel's data (*Z. angew. Chem.*, 1903, 16, 49) were published to controvert a statement by Winkler that the original values given by Bunsen (*Gasometrische Methoden*, 1877, p. 37) were too high, and as Göckel's results were in fair agreement with Bunsen's, they have been accepted, as stated above, in preference to the results obtained, using a different method of measurement, and published later, by Winkler (*Z. angew. Chem.*, 1903, 16, 372.)

The *International Critical Tables* (Vol. I, p. 72) give data from which the meniscus correction can be calculated for mercury in tubes of known diameter and with varying heights of meniscus. For any given diameter of tube the meniscus correction with a flat meniscus may be only one-tenth of the correction when the meniscus is curved, and consequently there is a grave objection to the use of mercury for calibration purposes. Mercury is unsuitable because its surface tension, and therefore the shape of the meniscus, is liable to be seriously altered by the presence of traces of impurities, and also because, owing to irregularities in the agitation of the mercury in the tube, even when the tube is clean otherwise than by the adhering layer of moisture, the angle of incidence of the mercury surface with the walls of the tube may vary within wide limits, influencing the shape of the meniscus thereby. There is, besides, the possibility that small air pockets will remain between the mercury and the glass at the angular corners at the bottom of sediment tubes.

No data are given in the *International Critical Tables* directly connecting the meniscus correction for water with the diameter of the tubes, but a table is given in Vol. I, p. 73, correlating values of $g\rho\frac{r^2}{\gamma}$ with $\frac{V}{r^3}$ computed from tables, derived from theoretical considerations, by Bashforth and Adams in "Capillary Action," for a liquid with meniscus concave upwards, and angle of incidence of liquid surface with cylinder = 0° , from which a table of meniscus corrections for water can be interpolated, where

- V = volume of meniscus = meniscus correction.
- r = radius of circular tube.
- g = acceleration of gravity.
- ρ = difference between specific gravities of air and water.
- γ = surface tension.

and the angle of incidence = 0° infers the use of thoroughly cleaned glass surfaces.

The following table gives the values of the meniscus correction for water at 20° C. in clean glass tubes of circular cross-section for various diameters interpolated from these data. The values for the smaller tubes given in the table are available for calibration of most of the sediment tubes in use, and the larger values may be of use in calibration of gas apparatus.

For comparison, the other published values quoted above are also shown on the table, along with the values of $1/3\pi r^3$.

MENISCUS CORRECTION.

Water at 20° C. Angle of incidence at Surface=0°.

Diameter of Tube. mm.	Meniscus correction.					$1/3\pi r^3$. ml.
	Bashforth & Adams' Data. ml.	Treadwell & Hall Quantitative Analysis. ml.	Sutton's Volumetric Analysis ml.	Winkler, <i>Z. ang. Ch.</i> ml.		
1.0	0.00013		0.00105	0.00013	0.00013	
1.5	0.00048					
2.0	0.00103		0.00215	0.00101	0.00105	
2.25	0.00145					
2.50	0.0020					
2.75	0.0026					
3.00	0.0033	0.006	0.00465	0.00318	0.0035	
3.25	0.0042					
3.5	0.0052					
3.75	0.0063					
4.0	0.0076	0.010	0.0072	0.0070	0.0084	
4.5	0.0106					
5.0	0.0142	0.0155	0.0130	0.0128	0.0164	
6.0	0.0234	0.022	0.0195	0.0206	0.0283	
7.0	0.0353	0.0305	0.0310	0.0308	0.0449	
8.0	0.0498	0.0405	0.0420	0.0432		
9.0	0.0666	0.0530	0.0570	0.0592		
10.0	0.0858	0.0670	0.0720	0.0778		
11.0	0.1073	0.0835	0.0950	0.0988		
12.0	0.1309	0.1020	0.1180	0.122		
13.0	0.1566	0.1225	0.1315	0.146		
14.0	0.1830	0.1445	0.1455	0.172		
15.0	0.2104	0.1680	0.1715	0.201		
16.0	0.2390	0.1935	0.1975	0.227		
17.0	0.2679	0.2205	0.2215	0.254		
18.0	0.298	0.2495	0.2460	0.283		
19.0	0.327	0.2800	0.2600	0.312		
20.0	0.356	0.3120	0.2740	0.339		

The most reliable values are those obtained from Bashforth and Adams' work, and they are closely in accord with the values to be expected from other theoretical considerations. All the published results determined by experiment suffer from the practical difficulties involved in the determinations, and are low for wide tubes, but Göckel's and Schloesser's results are very high for narrow tubes. Winkler's results, however, are closer to the theoretical values over the whole table and are extremely good for the narrowest tubes.

The magnitude of the meniscus correction is always less than $1/3\pi r^3$, but approximates to that value when the tubes are narrow. Bashforth and Adams' data show that the values obtained by using the formula $1/3\pi r^3$ for tubes of 2.0, 1.0 and 0.6 mm. diameter are, respectively, 2.4, 0.5 and 0.2 per cent. too high.

For tubes narrower than 1 mm. diameter it is obvious that the corrections can be calculated by assuming that the meniscus surface is a perfect hemisphere, and by using the formula $1/3\pi r^3$.

The correctness of the values applied in calibration does not affect many gas analyses, where, as a rule, small quantities of gas are measured by difference at parts of the burettes where the same correction applies to both readings, but it is of great importance in the calibration of sediment tubes where the total volume is required, and, unfortunately, it is just at the part of the tables where these measurements are affected that the published data show the greatest divergence.

For example, the amounts of sediment from certain liquids and of insoluble dust in air found in practical determinations are of importance at volumes of 0.010 ml. and 0.0010 ml. If the 0.010 ml. were measured in a tube of 3 mm. diameter and the volume noted by a mark, and, after cleaning and drying the tube, the volume of water required to fill to this mark were determined, the actual volume would be $0.010 + 0.0033 = 0.0133$ ml. Applying the correction given in Treadwell and Hall's book, however, namely, 0.006 ml., the apparent volume would be 0.0073 ml., and with Sutton's correction it would be 0.00875 ml.—errors of 27.0 and 12.5 per cent., respectively. The corresponding error in the calibration of 0.0010 ml. in a tube of 1 mm. diameter, using Sutton's correction, is much greater, the volume plus meniscus being 0.00113 ml., the correction 0.00105 ml., and the difference 0.00008 ml., which is less than one-tenth of the volume actually measured.

Some tubes calibrated for this purpose can be seen by inspection to be incorrect, probably from this cause, at the lowest graduation. The same error occurs, of course, at every graduation and, if the Treadwell and Hall meniscus correction has been used in calibrations of a tube of 3 mm. diameter, the volumes corresponding with marks at 0.010, 0.020, &c., ml. are actually 0.0127, 0.0227, etc., ml.

No attempt has been made in this paper to estimate the degree of accuracy which can be reached in the application of the theoretical values here given to the calibration of vessels. The errors in the values hitherto published, however, are much greater than those arising in practical work.

I have to thank Dr. S. Sugden for his help in confirming the meniscus corrections calculated above, and Sir Robert Robertson for permission to publish this paper.

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STRAND, W.C.2.

The Composition of Irish Winter Butter.

By P. S. ARUP, M.Sc., F.I.C., A.C.G.I.

(Read at the Meeting, October 2, 1929.)

THE fact that genuine Irish winter butter gives abnormal results on analysis has long been known, and was last demonstrated by Brownlee in 1925 (*Proc. Royal Dublin Soc.*, 18, [N.S.], 49). As is well known, calving takes place almost exclusively during one season of the year in Ireland, and abnormally low Reichert-Meissl values are observed at the end of the lactation period. It has been pointed out on several occasions in the Journal of the Department of Agriculture and Technical Instruction, both by Mr. G. Brownlee, B.Sc., F.I.C., and by Mr. A. Poole Wilson, Chief Inspector in Dairying of the Department, that, under these conditions, the assumption of the minimum standard of 24 for the Reichert-Meissl value is likely to lead to unjust prosecutions. As there still appears to be a tendency to apply this standard in too rigid a manner, it was decided by the Department of Agriculture to extend these investigations, and also to examine the validity of the Avé-Lallemant test as a criterion of genuineness for butter with abnormally low Reichert-Meissl values. It is stated in some standard text books that the Avé-Lallemant value may be so used, although Brownlee (*loc. cit.*) has thrown considerable doubt on the validity of this claim.

A total of 310 samples of cream or butter was taken from 30 creameries and 2 agricultural schools in the Irish Free State by Inspectors of the Department of Agriculture in such a way that the genuineness of the samples could be guaranteed. The creameries were sampled during the period from October 27th, 1927, to March 31st, 1928, as nearly as possible at fortnightly intervals.

Most of the samples were taken as cream and, except in the case of those from the agricultural schools, they represent the mixed milk of numbers of herds. The figures obtained are, therefore, likely to show less variation from the normal than would have been the case if single herds had been sampled; they are, however, quite comparable with the figures obtained by Brownlee (*loc. cit.*).

SEPARATION OF FAT.—It was found convenient to separate the fat from the cream samples by first freezing them, whereby the cream emulsion was broken, and then warming them to about 60° C. The fat then collected in a clear layer which could easily be dealt with. In a few cases where the fat globules in the cream were exceptionally small, as may be the case at the end of the lactation period, it was necessary to repeat the freezing and heating in order to obtain a good separation.

TABLE A.
FORTNIGHTLY AVERAGES.

Period.	No. of samples.	Maximum.				Minimum.						
		R.M.	Pol.	K.	Refract. Zeiss° at 40° C.	R.M.	Pol.	K.	Refract. Zeiss° at 40° C.			
27/10/27-15/11/27	37	24.96	1.71	18.17	44.7	26.8	2.40	19.5	23.0	1.35	17.2	42.3
16/11/27-30/11/27	34	24.23	1.74	17.65	44.4	28.2	2.70	21.7	21.9	1.40	15.9	41.8
1/12/27-15/12/27	24	23.80	1.68	17.77	44.2	29.7	2.85	20.9	20.8	1.15	15.7	41.5
16/12/27-31/12/27	22	23.81	1.75	17.76	43.6	28.8	2.45	21.7	20.4	1.35	14.6	41.9
1/ 1/28-15/ 1/28	24	24.65	1.88	18.20	43.8	28.9	2.95	20.6	21.6	1.60	15.9	42.0
16/ 1/28-31/ 1/28	40	25.77	1.80	19.06	44.2	29.4	2.85	23.0	22.7	1.45	16.8	41.7
1/ 2/28-15/ 2/28	32	26.98	1.89	19.81	44.1	31.9	3.20	22.0	24.4	1.60	17.2	42.9
16/ 2/28-29/ 2/28	30	28.55	2.10	21.18	44.1	31.6	3.05	24.3	25.2	1.55	17.8	43.5
1/ 3/28-15/ 3/28	35	29.52	2.03	21.60	44.1	32.9	2.85	23.6	25.1	1.40	18.6	43.2
16/ 3/28-31/ 3/28	32	30.11	2.12	21.71	44.0	32.7	3.00	23.8	26.7	1.45	18.3	43.2

TABLE B.

Creamery.	Date.	R.M.	Pol.	Kirsch.	K. as percent. of R.M.	Refract. Zeiss° at 40° C.	Saponification value.	Avé-Lallement value.
B	23/12/27	20.6	1.85	15.1	73.3	45.0	220.0	+6.5
C	14/12/27	20.8	1.50	16.0	77.0	44.8	220.1	+9.3
C	23/11/27	21.9	1.45	16.5	78.6	43.2	220.9	+14.0
D	14/12/27	21.6	1.35	15.7	72.7	44.5	220.9	+11.9
E	19/12/27	21.2	1.45	16.5	77.8	43.8	219.7	+14.0
F	21/12/27	21.6	1.40	16.3	75.4	43.9	222.9	+14.1
G	7/ 1/28	21.7	1.60	15.9	73.3	43.9	220.9	+13.6
H	7/ 1/28	21.6	1.60	16.4	75.9	44.2	225.0	+0.6
B	16/ 1/28	21.7	1.70	16.3	75.1	45.0	225.3	+4.3
I	23/11/27	22.6	1.65	15.9	70.0	44.1	227.7	+5.3
I	16/12/27	22.8	1.70	17.3	76.0	43.8	227.7	+8.1
J	22/12/27	22.3	1.50	17.1	76.7	44.6	225.0	+3.5
K	16/12/27	22.9	1.80	17.5	76.4	43.3	221.0	+11.7
L	31/12/27	23.1	1.80	18.0	77.9	44.4	224.4	+8.4
M	14/12/27	23.8	1.90	18.5	77.7	44.0	224.4	+9.0
N	23/12/27	23.8	1.85	18.3	76.9	43.3	224.4	+8.7
O	14/12/27	24.8	1.65	19.2	77.5	44.1	225.5	+11.0
P	24/12/27	24.9	1.75	19.1	76.6	42.8	225.0	+7.6
Q	23/12/27	25.5	1.95	19.0	75.1	44.0	226.1	+7.7
R	2/ 1/28	25.6	2.00	19.0	74.5	44.2	235.0	+11.1
S	4/ 1/28	26.7	2.95	18.9	70.7	42.0	233.4	-13.3
S	28/ 3/28	31.4	2.55	22.4	71.4	43.7		

The fortnightly average results with maxima and minima are shown in Table A. Full particulars of the samples which were also tested by the Avé-Lallemant method are given in Table B.

REICHERT-MEISSEL VALUES.—The following table shows particulars of the number of samples giving Reichert-Meissl values under 24:

R.M.	Number of samples.	Per-centage.	Dates of samples.
Below 20 Nil	Nil	
20-20.9 incl.	.. 3	0.9	14/12/27 to 23/12/27
21-21.9 8	2.6	23/11/27 to 16/1/28
22-22.9 16	5.2	23/11/27 to 21/1/28
23-23.9 23	7.4	31/10/27 to 31/1/28
Total under 24 ..	50	16.1	31/10/27 to 31/1/28

The last sample with Reichert-Meissl value under 25 was taken on February 14th, and the last with a value under 26 on March 6th. The average dropped below 24 during a period including approximately the last 9 days of November and the first three weeks of December. All the samples giving Reichert-Meissl values below 24 occurred from October 31st to January 31st inclusive. During this period 184 samples were taken, the percentage of these showing Reichert-Meissl values below 24 being 27.2.

Brownlee (*loc. cit.*) found, in 1924-25, that all samples with Reichert-Meissl values below 24 occurred from October 26th to February 6th inclusive, and that, of the 75 samples taken during this period, 81 per cent. were below the standard of 24. Of the total number, 5 were below 20, as compared with none in the present (1927-28) series, and 20 were below 21, as against 3 in 1927-28. The twelve creameries sampled in 1924-25 were all included in the present series, and the difference between the two sets of figures points to an improvement in Irish Dairy farming, as a result of the activities of the Department under the Dairy Produce Act of 1924. The factors responsible for the change are: (1) A tendency to extend the calving period, and (2) a certain improvement in the treatment of the cows during the winter.

The samples from the Department's Agricultural Schools at Ballyhaise and Clonakilty in the present series, 20 in all, deserve special mention, for in no case did they give Reichert-Meissl figures below 26. This is explained by the fact that calving in these places is not confined to one season of the year, as is generally the case in Ireland, and also by superior conditions of feeding and shelter. Similar effects are noted with regard to the Polenske values below.

POLENSKE VALUE.—The maximum value recorded was 3.20 in connection with a Reichert-Meissl value of 31.4, and the minimum 1.15 in connection with a Reichert-Meissl value of 22.2.

The following Table shows average, maximum, and minimum Polenske values obtained with progressive Reichert-Meissl values:—

Number of samples.	R.M. (-0.5 +0.4.)	Polenske.			Variation between max. & min.
		Average.	Max.	Min.	
15	22	1.50	1.70	1.15	0.55
22	23	1.60	1.80	1.35	0.45
43	24	1.65	2.00	1.40	0.60
56	25	1.70	2.25	1.35	0.90
35	26	1.90	2.40	1.45	0.95
26	27	1.95	2.85	1.55	1.30
22	28	2.05	3.05	1.60	1.45
15	29	2.20	2.85	1.75	1.10
26	30	2.10	2.85	1.65	1.20
30	31	2.25	3.20	1.60	1.60

For Reichert-Meissl values of 22-26, inclusive, the average Polenske values agree very closely with those given by Bolton in his "Oils, Fats and Fatty Foods." For increasing Reichert-Meissl values above 26, the averages begin to fall below Bolton's figures, being 0.95 less at Reichert-Meissl 31.

All the creameries sampled, except the Agricultural Schools at Ballyhaise and Clonakilty, tended to produce butters showing Polenske values below the normal; this is reflected by the somewhat large differences between maximum and minimum values in the above table for Reichert-Meissl values of 26 and over; all the maximum Polenske values recorded, however, fall within 0.5 of the standards given by Bolton, thus confirming his criterion indicating freedom from adulteration with coconut or palm-kernel oils. In contra-distinction to the rest of the creameries sampled, 10 samples from Ballyhaise averaged:—Reichert-Meissl value, 28.3; Polenske value, 2.5. Ten samples from Clonakilty averaged Reichert-Meissl value, 29.0; Polenske value, 2.75; that is, they gave normal Polenske values, for reasons similar to those discussed in connection with Reichert-Meissl values above.

KIRSCHNER VALUE.—This was determined by the standard method, with the use of aluminium wire in the distillation. The minimum value recorded was 14.6 in connection with a Reichert-Meissl value of 20.4, and the maximum was 24.1 in connection with a Reichert-Meissl value of 32.7. The average Kirschner value of all the samples was 73.4 per cent. of the average Reichert-Meissl value. On individual samples, this percentage varied from 68.0 to 79.6, but showed no co-ordination with variations in the Reichert-Meissl value or other factors.

The relationship between Kirschner and Polenske values is shown in the following table:

No. of samples.	Kirschner value (-0.5 +0.4.)	Polenske value.			Variation between max. & min.
		Average.	Max.	Min.	
30	17	1.55	1.85	1.15	0.70
69	18	1.70	2.40	1.35	1.05
67	19	1.85	2.95	1.45	1.50
27	20	1.95	3.05	1.60	1.45
22	21	2.15	2.80	1.55	1.25
39	22	2.15	2.85	1.60	1.25
25	23	2.20	3.00	1.65	1.35

The agreement with the figures published by Bolton and Revis and Richmond is not so close here as in the case of the relations between the Reichert–Meissl and Polenske values, and in several cases the maximum Polenske values are too high to fit in with the criterion for determining the presence of coconut oil or palm-kernel oil.

AVÉ-LALLEMANT VALUE.—Twenty-two samples with Reichert–Meissl values varying from 20.4 to 25.5 showed Avé–Lallemand values varying from +14.1 to –3.5, only one sample giving a negative value. Two samples having Reichert–Meissl values of 26.7 and 31.4 showed Avé–Lallemand values of –11.1 and –13.3, respectively (see Table B). Brownlee (*loc. cit.*) found values varying from –25.0 to +10.4, 20 samples out of a total of 112 giving positive results.

The conclusion of Brownlee that the Avé–Lallemand value cannot be taken as a criterion for distinguishing between genuine butters having low Reichert–Meissl values on the one hand, and adulterated butters of higher Reichert–Meissl values on the other, is confirmed here. It would appear that butters with low Reichert–Meissl values had not been sufficiently investigated in this connection before the matter was taken up by Brownlee, and that the Avé–Lallemand value, in common with most of the other commonly determined figures, merely tends to serve as a confirmation of the Reichert–Meissl value.

SAPONIFICATION VALUE.—In 24 samples this varied from 219.4 to 235.0, thus confirming the usually accepted limits for pure butter.

THE COMPOSITION OF IRISH WINTER BUTTER, 1928–9.

A series of analyses similar to that reported for the winter season of 1927–8, was carried out for the season of 1928–9. The results confirm those previously obtained, so that a brief summary will suffice. Out of a total of 270 samples, representing 36 creameries and 3 agricultural schools, taken from November 1st, 1928, to February 23rd, 1929, those showing R.M. values below 24 were as follows:

REICHERT–MEISSL VALUE.

R.M.	No. of Samples.	Percentage.	Dates of Samples.
Below 20	Nil	Nil	
20–20.9	3	1.1	5/12/28 to 17/12/28
21–21.9	17	6.3	19/11/28 to 3/ 1/29
22.0–22.9	34	12.6	1/11/28 to 18/ 1/29
23.0–23.9	34	12.6	1/11/28 to 25/ 1/29
—	—	—	—
Total	88	32.6	1/11/28 to 25/ 1/29

The average figures for fortnightly periods were as follows:

Period.	No. of samples.	Average.	
		R.M.	Pol.
November 1st-15th	28	24.2	1.69
„ 16th-30th	37	23.3	1.61
December 1st-15th	32	22.9	1.63
„ 16th-31st	31	23.5	1.78
January 1st-15th	34	25.5	1.85
„ 16th-31st	36	26.5	1.79
February 1st-13th	28	27.0	1.75
„ 14th-23rd	30	28.3	2.00

The unusually cold weather which prevailed all over the country from the 11th to the 17th of February had no noticeable effect in checking the upward tendency of the Reichert-Meissl values, and it may be concluded that the predominating factor influencing these values is the lactation period.

POLENSKE VALUE.—The minimum recorded was 1.30 in connection with R.M. values of 21.1 and 24.9. The maximum was 3.40 with R.M. of 29.2. All the Polenske values taken in connection with their corresponding R.M. values fell within the limits generally laid down in the literature for genuine butter. When the R.M. values increase during the early part of the year, the Polenske values do not increase at the same proportionate rate, and are thus somewhat below the average. In the case of the samples from the three agricultural schools, however, the Polenske values were higher, and, generally speaking, about the normal. In these particulars the experience of last year is confirmed.

KIRSCHNER VALUE.—This was determined on 136 samples, mostly those having R.M. values below 24, and was found to vary from 67.3 to 81.2 when expressed as a percentage of the corresponding R.M. value. It was not found possible to trace any connection between these variations and any other factor.

BRINE-SOLUBLE AND BRINE-INSOLUBLE VALUES.—These were determined by Elsdon and Smith's modification of Gilmour's method (*ANALYST*, 1927, 52, 317). The distillation process is the same as in the Reichert-Meissl-Polenske process except that 100 c.c. are distilled instead of 110 c.c., so that the total volatile acids were consistently lower than in the Reichert-Meissl process. In order to ascertain whether the salting-out process gives more consistent results than the usual method, the following comparisons were made:—Seventy samples showed ordinary Polenske values varying from 5.5 to 10.4 per cent. of the total volatile acids, and brine insoluble values from 10.1 to 23.8 per cent. The seven highest and seven lowest Polenske percentages varied from 5.5 to 5.8, and from 8.3 to 10.4 respectively, whilst the corresponding percentage figures for the brine-insoluble were 10.1 to 12.0 and 17.7 to 23.8, respectively.

The following table shows some typical results obtained with butter of low Reichert-Meissl values; the brine-insoluble values are about twice the Polenske values, as Elsdon and Smith found to be the case with butters of higher Reichert-Meissl values. The brine soluble values are slightly higher than the corresponding

Kirschner values. As a measure of the volatile acids in pure butter, the brine method does not appear to offer any particular advantages over the Reichert–Meissl–Polenske method, but there is a possibility that it might do so in the case of mixtures containing palm nut or coconut oils. The method was of course primarily designed for the estimation of butter in margarine, and for this purpose it offers some advantages over the Kirschner method, being simpler and less liable to experimental error.

Date of sample.	R.M.	Polenske.	Kirschner.	Kirschner as per cent. of R.M.	Brine.		Refractive index, Zeiss ^o at 40° C.
					Sol.	Insol.	
5/12/28	20.8	1.50	16.2	77.9	17.6	3.20	46.9
17/12/28	20.7	1.70	14.5	70.0	17.6	2.35	46.6
„	20.8	1.50	14.5	69.7	17.3	2.55	46.9
19/11/28	21.8	1.35	16.1	74.0	19.0	2.55	45.2
26/11/28	21.5	1.45	16.0	74.3	17.9	2.55	47.0
1/12/28	21.3	1.40	16.4	76.9	18.4	2.20	46.9
3/12/28	21.8	1.50	15.6	71.5	18.2	2.80	46.9
„	21.1	1.55	17.1	81.2	18.6	3.20	46.9
„	21.7	1.65	16.8	77.3	18.8	2.45	46.9
5/12/28	21.5	1.35	17.2	80.2	17.5	2.85	46.4
7/12/28	21.9	1.65	16.5	73.8	18.0	2.45	45.5
10/12/28	21.5	1.55	16.2	75.3	17.8	2.60	46.9
12/12/28	21.1	1.50	16.4	77.7	17.1	2.25	46.8
„	21.5	1.60	16.0	74.6	17.8	2.40	46.7
18/12/28	21.7	1.60	15.9	73.3	18.8	2.75	45.8
19/12/28	21.3	1.50	15.4	72.3	18.7	2.10	46.4
22/12/28	21.1	1.30	15.1	71.5	18.5	2.40	45.9
24/12/28	21.7	1.60	15.2	70.0	18.5	3.05	45.8
31/12/28	21.9	1.70	16.3	74.6	18.7	2.40	45.5
3/ 1/29	21.6	1.65	15.5	71.6	18.4	3.00	—
1/11/28	22.8	1.50	17.6	77.2	19.0	3.05	44.8
„	22.6	1.60	16.8	74.5	17.4	3.20	45.4
19/11/28	22.3	1.45	17.2	77.3	19.3	2.40	46.3
„	22.7	1.40	16.7	73.7	19.4	2.70	47.0
„	22.6	1.45	16.1	71.3	19.0	2.75	45.5
„	22.1	1.45	16.1	75.3	19.0	2.50	45.7
„	22.8	1.65	17.7	77.9	19.4	2.95	45.7

I wish to express my thanks to the Department of Agriculture, Irish Free State, for permission to publish the above matter.

DEPARTMENT OF AGRICULTURE,
BUTTER TESTING STATION, DUBLIN.

DISCUSSION.

The PRESIDENT said that it was very disturbing that we should have winter butters giving such abnormal values. It raised difficulties in the interpretation of analytical results. He was much obliged to Mr. Arup for coming from Ireland to read this paper. He referred to many members who regretted their inability to be present, and read some observations sent by Mr. G. D. Elsdon. They were

fortunate in having with them Mr. F. Dickinson, of the Chemical Research Division, Ministry of Agriculture, Northern Ireland, who had been so good as to come from Ireland for this meeting.

Mr. F. DICKINSON (Department of Agriculture, Northern Ireland), speaking also on behalf of Dr. G. S. Robertson, said that it was interesting that both Northern Ireland and the Free State should have been conducting independently, and without previous knowledge of each other's activities, an investigation as to the behaviour of butter towards the Reichert-Meissl test. Both investigations appeared to have begun about the same time; that in Northern Ireland started in June, 1927, and was still in progress, whilst Mr. Arup's started in November, 1927. They had also been examining at regular intervals butter from seven creameries, three of the Ministry's farm schools, where a uniform milk yield was maintained, throughout the year, and the influence of lactation was, therefore, minimised; and also farm butter produced from the herds of seven private breeders, included in which were Jersey, Kerry and Crossbred Shorthorn herds.

In the main, their results were in keeping with those obtained by Mr. Arup. The results of the two years' investigation showed that there was a big drop in the Reichert-Meissl value in August, and that during 1927-28 that value was below 24 during September, October, November, and December. During January there was a marked recovery, and from then onwards the figure remained normal. The corresponding curves for the three schools and the private herds were similar; and as a more or less even flow of milk was maintained at these three Institutions, it was difficult to agree with Mr. Arup that the lactation period was mainly responsible for the low Reichert-Meissl values during September to January. It was because it was clear to them that some factor other than the period of lactation was involved, that they decided to carry on the investigation over a period of years before publishing the figures.

In this connection the results for 1928-29 were interesting. The Reichert-Meissl figures were very much higher. Mr. Arup accounted for the marked improvement in Free State butter by crediting it to the beneficial activities of the Free State Dairy Produce Act. Northern Ireland had not yet a Dairy Produce Act; nevertheless, there was manifested the same tendency towards an extension of the calving period and better feeding in the winter. Such changes, however, were only gradual, and it was inconceivable that they could account for the very marked improvement in the Reichert-Meissl values for the season 1928-1929, when compared with 1927-1928.

Some other factor was clearly operating, possibly a climatic factor which influenced the nutritional value of the grass and hay. There was a suggestion from their results that a shortage of minerals might be associated with the production of butter-fat with a low Reichert-Meissl value.

One other point might be of interest to members. They were considering, pending the conclusion of the investigation, the issue of a monthly Reichert-Meissl value, which would be circulated to the Public Analysts in Northern Ireland, the number being based on the determinations on butter made at Northern Ireland creameries under the supervision of the Ministry's staff.

Mr. E. R. BOLTON, in expressing his appreciation of the utility of the figures the author had given, observed that he could not help regarding them with mixed feelings. Although some criticism might be made of the method of separating the fat, he himself was clearly of opinion that the method, though unfortunate, did not affect the accuracy of the figures, which he accepted without question.

From the scientific point of view, it was interesting once more to have confirmation of the fact that, when cattle were subjected to certain conditions, they

actually produced a butter-fat that was not of the normal composition of the butter everyone was accustomed to receive when they asked for a pound of butter over the counter. This, he thought, was indeed very unfortunate, as he feared the publication of this paper would have the effect of causing quite unjustified damage to the Irish butter trade. Everyone knew that Irish butter was an extremely good product; but if the public were now to be told that during certain times of the year it became an abnormal product, and would, by the tests already accepted, be held to be adulterated, it would be very difficult to persuade them that this abnormality might not also mean inferiority.

At this point he would like to defend certain tests upon which he had always placed reliance, and, in particular, the Avé-Lallemant test. This test, in his opinion, was a rapid and reliable method of finding out whether a butter was, or was not, of normal composition and unadulterated. It was not vitiated by the presence of mixtures of coconut with other fats, which vitiated certain other tests. In the case of these Irish butters the Avé-Lallemant test showed that the butters were not of normal composition; he regarded this as confirming, rather than shaking, his confidence in the test.

The analyst, therefore, was faced with a very difficult position, and if the analyst were to become an advocate—which he should never be—he would find a great deal to say. On the one hand, he might claim that if a cow were not treated in a normal manner the butter-fat which resulted could not be regarded as the product that the public expected when they demanded butter. If, on the other hand, he wished to justify this butter, he might say that the product had come from the animal, nothing had been added to it, and it should be regarded as genuine butter.

It, therefore, became more an ethical question than an analytical one, and he asked Mr. Arup if he could give the meeting some guidance on the light in which, in his opinion, this question should be regarded. Mr. Arup had said of the cattle, "as a rule they are very badly fed indeed," and what he (Mr. Bolton) asked was whether good feeding, better environment, and a spreading-out of the calving period would not have the effect of rendering this butter normal; and, in view of the fact that the Irish Dairy Produce Act, 1924, had (as Mr. Arup had said) brought about a great improvement, he enquired whether it was, or was not, a fact that the public might expect the farmers to put this butter question right themselves (and relieve the analyst of the whole question of deciding what should be done with an admittedly abnormal butter) by the simple process of removing such abnormal butters from the market by improving their methods of farming.

Mr. W. WRIGHT (Inspector of New Zealand Dairy Products, London, of the Dairy Division, New Zealand Department of Agriculture) said that he felt that, although he was the guest of the Society that evening, he was rather an outsider, since he was more conversant with the technology of dairying than with analytical chemistry. He had been very interested in the subject which had been under review that evening. With regard to the irregularity of the butter-fat during the period mentioned, he pointed out that there were several factors which, in his opinion, would affect the butter-fat in milk. For instance, general health and care of the dairy stock, climatic conditions, such as abnormal rainfalls, lack of sunshine and cold windy weather, the quality of the pastures, and also method of feeding and treatment of the stock during the lactation period. As the lactation period of cows progressed there did appear to be a change which took place when the lactation period was drawing to a close, and for that reason the milk and butter were at such times less attractive or palatable for human consumption. He felt that before steps were taken to prosecute in the matter of faults in the constituents of milk, butter or cheese, there should be a reasonable margin of error

allowed in chemical analysis. Owing to the fact that there was such a variable percentage of butter-fat and solids-not-fat in milk, and since changes in the butter-fats might be brought about by abnormal conditions, products that were absolutely free from adulteration might be of such quality that, when analysed, they might be classified as having been adulterated. There was no doubt that Mr. Arup's paper had opened up a very wide question, and, if he might make the suggestion, he thought that, when possible, in future observations regarding the fat percentage of butter, a record should be kept of the condition of the animals from which the milk was obtained, and of the pastures, feeding and climatic conditions during the research period. In his opinion, it was probable that valuable data would thus be obtained which would do much towards solving the problem under discussion.

Mr. A. MORE said that the problem for the analyst was to say whether a butter was genuine or not, and for this purpose the Reichert-Meißl value was the most important factor. The work of the Departmental Committee in 1901-2 had shown that genuine butter from Ireland, and also from England and Scotland, had low Reichert-Meißl values at the same time of year as those shown in the present paper, and that Committee had suggested the adoption of a value of 24 as a presumptive standard only. The chemist was apt to be misled in judging the quality of butter by the Reichert-Meißl value, but there was no evidence to support the assumption that butter of low Reichert-Meißl value was necessarily inferior in quality. This paper would have the effect of preventing prosecutions based solely on a presumptive standard. He did not think that a positive Avé-Lallemant value was a criterion of adulteration. He produced a chart of Avé-Lallemant's original results (*Z. Nahr. Genussm.*, 1907, p. 321), in which all the values were negative, but the lowest Reichert-Meißl value was 24.6, and the curve passed over, if continued, to positive values, at a Reichert-Meißl value of 25. Positive results which he had obtained on butters with Reichert-Meißl values of 21 agreed with those of Mr. Arup.

Mr. K. A. WILLIAMS remarked that the general tendency of the analytical figures for poor butters was exactly the same as for adulterated butters. In particular, he had found that the relation between the Reichert-Meißl and Avé-Lallemant values, shown by Mr. More for butter-fats of varying quality, was identical with that for adulterated butter-fats. It followed that, at the present time the assumption of arbitrary limits was the only possible means available for deciding whether a sample was pure; he, personally, would welcome the discovery of a factor which would determine purity without reference to such limits.

Dr. H. E. COX said that the introduction of the factor "b-(200+c)" in the Avé-Lallemant process was artificial and misleading; the change of sign from - to + gave a false sense of security which was not warranted by the change of a few units in the barium oxide values. One could not be sure of saponification values nearer than about 1 unit in terms of potassium hydroxide, and a larger figure in terms of barium oxide. He disagreed with the view that the butter was inferior; the only point to his mind, as a Public Analyst, was whether the purchaser was prejudiced, and it could not be said that he was, simply because he got a little less butyric acid and a little more of the higher fatty acids, as at present we knew nothing of their relative dietetic values. He urged the need for a quick method for the determination of the melting point of the sterol acetates, workable on the small amount of fat usually available to the Public Analyst, after he had made his other tests.

Mr. MORE here offered to let Dr. Cox know the details of a method which he had found to give satisfactory results with 15 grms. of fat, and which had been

given to him by Dr. van Sillevoldt of the Butter Control Station, at Leiden, Holland.

The PRESIDENT remarked that there was no very certain relation between Reichert value and commercial quality, but it seemed that these abnormally low Reichert values were associated with bad farming practice, semi-starvation of the cattle, and so forth. He supposed that the more a natural product like butter was investigated, the greater was the probability of the disclosure of occasional abnormality. It really came to this, that by abnormal, and generally undesirable, conditions, abnormal butters could be produced. If it could be shown, and the paper and the discussion did so show, that by proper farming normal, and not abnormal, butter was obtained, then it seemed to be desirable in the public interest that a minimum Reichert value should be established by law. He hoped that the Ministries of Agriculture of the Free State and of Northern Ireland, and of England and Scotland too, would use their influence to ensure that farming should be such that the produce was what was given by good farming. Extreme insistence on the principle that anything that came from the cow was "genuine" was damaging the public.

Mr. G. D. ELSDON (in a written communication) said that the Avé-Lallemant process had, unfortunately, not fulfilled the hope that it at first aroused, and Mr. Arup's work still further discouraged its use. The process was somewhat lengthy, and the figures obtained were sensitive to quite small experimental errors, and afforded very little assistance in coming to a final decision as to the genuineness of any particular sample. It was, of course, now firmly established that butter obtained from milk taken towards the end of the lactation period was quite likely to be deficient in volatile acids, but this fact should be taken as an exhortation to farmers to arrange their calving so that butters with low Reichert values should not be produced. It was never safe, of course, to report a butter as adulterated on the evidence of the Reichert value alone, unless this was considerably under 20. It was possible that some information might be obtained from the differences between the brine-insoluble figure and the Polenske figure, as this would be a measure of the volatile acids of high molecular weight. He had not, as yet, had an opportunity of examining this suggestion. It might also be valuable if Mr. Arup carried out some work on Irish butters on the lines followed by Atkinson (*ANALYST*, 1928, 53, 520).

Mr. ARUP, replying, said that with regard to the question whether low Reichert-Meissl values indicated poor quality in butter, samples had been examined by experts, with a view to determining this question, and it had been found that there was no connection at all between these factors. There was, therefore, no question of prejudice to the public, but the matter was one which might give some trouble to the analyst. He agreed with Dr. Cox that the Avé-Lallemant formula, giving, as it did, positive and negative values, invited judgments which might be too rigid. He would wish to see the whole problem attacked from a different point of view, as it appeared that the possibilities of volatile acid determination had been exhausted. Other butter-producing countries had experienced the same trouble, notably Holland, and it had been generally agreed that it arose in connection with the lactation period.

If it were a question of the addition of margarine to butter, the sterol acetate method was very useful, as vegetable oils or fats were sure to be contained in any margarine; and the use of hardened vegetable oils, now very common, did not, in his experience, vitiate the results of this test; hardened oils had largely come to replace animal fats. With the use of digitonin, the method was very convenient, and was capable of detecting as little as 2.5 per cent. of margarine.

He had been very interested in Mr. Dickinson's remarks; it was a remarkable coincidence that the two Ministries had been doing identical work, and he hoped that in future it would be possible for them to co-operate. He had not examined a large number of samples systematically before October of each year. In Ireland, cows were very much more dependent upon the grass than in many other countries, as very little roots and meal cakes were used, and so were dependent upon climatic conditions. The feeding at the agricultural schools during winter consisted of hay, with roots and palm-kernel cake. The average farmer only gave palm-kernel cake in a very few cases.

Reference to the paper would show that no attempt had been made to draw conclusions from a comparison of the results of 1927-8 with those of 1928-9, but the results quoted there were compared as a whole with those obtained by Mr. Brownlee for 1924-5. It was recognised that there would be very little use in comparing results of consecutive years, for reasons very similar to those mentioned by Mr. Dickinson.

A Study of the Methods of Determining Boron Compounds in Food and Drugs.

By A. SCOTT DODD, B.Sc., Ph.D., F.I.C.

(*Work done under the Analytical Investigation Scheme.*)

PART I. HISTORICAL REVIEW.

IN the early days of the Food and Drugs Acts, the officials charged with the detection of adulteration were chiefly concerned with the presence of boron compounds in quantities sufficient to be deemed injurious to health, and with their determination with sufficient accuracy to avoid challenge. In those days the methods were somewhat elaborate and crude, and, in the absence of the discovery of suitable conditions under which indicators could be employed, depended upon the formation of weighable compounds of boron.

THE DISTILLATION METHOD.—The separation of the boric acid from the organic constituents of food was then found to be most reliably effected by distillation in presence of methyl alcohol and an acid. This method is usually associated with the name of Gooch, but it appears to have originated somewhat earlier than Gooch's publication (*Proc. Amer. Acad. Arts and Sciences*, 1886, **22**, 167), as it is referred to by T. Rosenbladt (*Z. anal. Chem.*, **26**, 18). It is, however, quite possible that these investigators may have made the discovery independently.

For many years the distillation method was, and still is, recognised as affording accurate results, and chemists, though satisfied that all the boric acid had distilled, were anxious to ascertain the most reliable method of finally determining it in the distillate. As already mentioned, no trustworthy titration method had been devised, so the boric acid was at first determined gravimetrically.

FIXATION OF BORIC ACID.—T. Rosenblatt (*loc. cit.*) fixed it in the distillate by the addition of a weighed quantity of magnesia, evaporating and igniting. Gooch, recognising that magnesia did not fix the boric acid completely, recommended the use of caustic lime. Penfield and Sperry (*Amer. J. Sci.*, **30**, [iv], 222), in view of the difficulty of igniting to constant weight a comparatively large quantity of caustic lime, modified the process. Cassal (*ANALYST*, 1890, **15**, 375) suggested further improvements, but both modifications failed to remove the difficulty of igniting a gramme or more of lime to a constant weight in a platinum basin. Blount (*ANALYST*, 1891, **16**, 144) stated that the difficulty was overcome by using a muffle furnace.

The use of lime for fixing boric acid is due to H. Gilbert (*Report Anal. Chem.*, Vol. V, p. 375), so that the method attributed to Gooch is really a combination of Rosenblatt's distillation method and Gilbert's ignition process.

Otto Hehner (*ANALYST*, 1891, **16**, 141) investigated the use of other chemical compounds as substitutes for lime. He tried ammonia, but the results of his experiment merely confirmed the observation of Bodewig (*Z. anal. Chem.*, 1884, **23**, 149), that boric acid is volatile in presence of ammonia. By substituting sodium carbonate for ammonia, Hehner found it almost impossible to obtain constant weights. According to Bloxam, one molecule of boric acid displaces, on gentle ignition, one molecule of carbonic acid, but on strong heating (to red heat) it displaces from 1.5 to 2.3 molecules; while, according to Schaffgotsch, one equivalent of H_3BO_3 expels all carbonic acid from two molecules of sodium carbonate. Hehner's figures are more comparable with those of Bloxam, but show that sodium carbonate does not give reliable results.

Hehner found that one molecule of sodium phosphate (Na_2HPO_4) is capable of binding two molecules of H_3BO_3 , the resulting mass consisting of sodium metaphosphate and borax. He found that very good results may be obtained by the use of sodium phosphate, which has many advantages compared with lime.

EARLY VOLUMETRIC METHODS.—Investigators next turned their attention to the quest for a reliable volumetric method of estimating boric acid. Various indicators were suggested, but none gave satisfactory results. Permentier (*Compt. rend.*, **113**, 41) made two titrations, using two indicators—helianthin and litmus—and reckoned as boric acid the difference between the two titrations.

In 1878 Klein (*Bull. Soc. Chim.*, **29**, 195) first pointed out that additions of certain polyatomic alcohols and sugars had the effect of rendering boric acid solutions more acid. The explanation of such reactions was that combination takes place, with the production of stronger acids. Since then numerous researches have been made, which have added considerably to our knowledge of the subject, and it is now known that not only polyatomic alcohols and sugars form such combinations, but also that a large class of hydroxy compounds reacts similarly.

USE OF SUGARS AND POLYHYDRIC ALCOHOLS.—It was not until 1893 that the action of boric acid on sugars and polyhydric alcohols was made use of in the estimation of boric acid, when R. T. Thomson (*J. Soc. Chem. Ind.*, 1893, **12**, 432)

published his investigations. He found that, when glycerol was added to a solution of a borate, the acidity was increased until, when about 30 per cent. of glycerol, calculated upon the total amount of fluid, was present, the maximum acidity was reached and the total amount of boric acid was sharply indicated, phenolphthalein being the indicator. The end-point of the titration coincided with the entire conversion of the boric acid into sodium metaborate (NaBO_2). Thomson then intimated that he was experimenting on the applicability of his process to the determination of boric acid in food materials. The results of these investigations were published in 1895, and showed a method by which the organic and other interfering substances could be eliminated by ignition in presence of caustic soda and subsequent treatment with solutions of calcium salts. (*Glasgow City Anal. Repts.*, 1895, p. 3.)

K. Thaddéeff (*Z. anal. Chem.*, 1897, **36**, 568) devised a method of determining boron compounds which was really a modification of that of Gooch. It consisted essentially of distillation as methyl borate and fixation and weighing as potassium borofluoride. This method was, however, criticised as defective in two important points by F. A. Gooch and L. C. Jones (*Z. anorg. Chem.*, 1898, **19**, 417), who stated that accuracy can only be attained when the errors due to these defects neutralise one another. They suggested using lime with the addition of sodium tungstate as an absorbent, to prevent loss through the precipitate being hygroscopic.

The reliability of glycerol as an aid to titration, using a method attributed to Jörgensen, was tested by Beythien and Hempel (*Z. Unters. Nahr. Genussm.*, 1899, **2**, 842) and by H. Luhrig (*Pharm. Centralh.*, 1901, **42**, 50). The authors found that less accurate results were obtained by combining Gladding's method with that of Jörgensen than by using the latter alone.

OTHER METHODS.—Various more or less ingenious methods have been suggested, such as the colorimetric methods of C. E. Cassal and H. Gerrans (*British Food J.*, 1902, **4**, 210), of A. Hebebrand (*Z. Unters. Nahr. Genussm.*, 1902, **5**, 1044), and of Bertrand and Agulhon. There is also a gravimetric method with a special distilling tube, utilising the solubility of boric acid in ether saturated with water, which was devised by A. Partheil and J. A. Rose (*Z. Unters. Nahr. Genussm.*, 1902, **5**, 1049).

BORIC ACID IN CREAM, BUTTER AND MARGARINE.—As a result of the report of the Departmental Committee, dated 1901, permitting the use of a limited quantity of boric acid and borax in cream, butter and margarine, steps were taken by some investigators to devise a rapid and accurate method of estimating boric acid in these foods. The ignition of such highly fatty materials presented certain difficulties, and was open to criticism on the grounds that some of the boron compounds were volatilised thereby, even if an excess of alkali was present. T. Macara (*ANALYST*, 1913, **38**, 142) and C. R. Bagshaw (*ANALYST*, 1918, **43**, 138). Richmond and Harrison (*ANALYST*, 1902, **27**, 179) eliminated the difficulty of igniting by merely separating with chloroform and water and taking an aliquot part of the aqueous extract for the estimation. This method, though said to be

accurate, occupied a considerable amount of time; so the authors devised a still more rapid process, which has since been used extensively by dairy chemists. In this method, the boric acid, after treatment, can be titrated without the fat being first removed. Another rapid process, based on coagulation of the milk or cream with copper sulphate and determination of the boric acid in the aqueous portion, is recommended by Richardson and Walton (*ANALYST*, 1913, 38, 140). Many other methods have been devised, with the same end in view, but no one hitherto seems to have made any attempt to investigate fully the effect of igniting boron compounds in presence of varying proportions of fats and oils.

MODIFICATIONS OF TITRATION METHODS.—Various modifications of the methods of titrating boric acid have been suggested. E. B. R. Prideaux (*Z. anorg. Chem.*, 1913, 83, 362) stated that boric acid might possibly be titrated with tolerable exactness by the selection of a suitable indicator, and recommended tropaeoline O. B. H. St. John (*Amer. J. Pharm.*, 89, 8–10) stated that methyl red was a better indicator than methyl orange in the neutralisation of borate solutions previous to the titration of the boric acid in the presence of glycerol and phenolphthalein. J. Prescher (*Z. Unters. Nahr. Genussm.*, 1918, 36, 283) investigated the use of various indicators, and found that, for the final titration, after using either glycerol or mannitol, the most suitable indicator is phenolphthalein. For the neutralisation of borate solutions other indicators have been recommended, such as paranitrophenol, W. Hertz (*Z. anorg. Chem.*, 33, 353) and Sofnol Indicator No. 1, by myself (*ANALYST*, 1927, 52, 459).

SUBSTITUTES FOR GLYCEROL.—Much research has also been carried out, with a view to ascertaining what substances can be substituted for glycerol. Some doubt seems to exist whether a definite compound is formed when glycerol is mixed with a solution of boric acid. The acid complex, formed by the addition of glycerol to boric acid solutions, has been named glyceryl-boric acid and given the formula $(C_3H_5O_2OH)B(OH)_3$, but some investigators maintain that no compound is formed (R. Dubrisay, *Compt. rend.*, 1921, 172, 1658). The rise in the electrical conductivity observed in solutions of boric acid and poly-hydroxy compounds gives an indication of the stability of the compound formed. Now, glycerol, when added to a solution of boric acid, does not exhibit a very marked positive effect on the conductivity of the solution. This bears out the contention of Dubrisay, and shows clearly that, if a compound is actually formed by the glycerol and boric acid, it is very unstable in aqueous solution.

Thomson (*loc. cit.*) tried to replace glycerol by dextrose and cane sugar, but without success. Vedam (*J. Pharm. Chim.*, 1898, 6, 8, 109) used mannitol, and found that with its use a sharper end-point is obtained than when glycerol is employed.

The stability of the compound formed by boric acid and mannitol is emphasised by the marked increase in electrical conductivity imparted to boric acid solutions by the addition of mannitol, and also by the fact that for the same quantity of boric acid very much less mannitol than glycerol is required for the purpose of titration.

Agno and Valla (*Gazz. Chim. Ital.*, 1913, **43**, 11, 163), from solubility measurements, concluded that mannitol unites with boric acid in equimolecular proportions. Salts of complex bodies, formed by the union of boric acid with mannitol, sorbitol, and dulcitol, have actually been prepared by Grün and Nossoivitch (*Monatsh.*, 1916, **37**, 409), and, by using the same method, Gilmour (*ANALYST*, 1921, **46**, 3) has prepared the sodium derivative of a complex formed from laevulose and boric acid.

G. Van B. Gilmour (*loc. cit.*) was able to titrate boric acid successfully in the presence of laevulose, dextrose and cane sugar, but found that it was impossible to carry out the titration with lactose. Weak combinations require a large excess of the hydroxy compound; otherwise the complex is hydrolysed before the proper end-point is reached. Laevulose gives excellent results, but the high price of the pure sugar renders its use prohibitive for technical purposes. Invert sugar, on the other hand, is cheaply prepared, and is an excellent substitute. Gilmour's claim to be the first to advocate the use of invert sugar was disputed by J. A. M. Van Liempt (*ANALYST*, 1926, **51**, 293), who pointed out that the use of invert sugar for this purpose had already been suggested by M. Boeseken (*Proc. Roy. Acad. Amsterdam*, 1917, **26**, 3), and worked out by himself (*Rec. Trav. Chim.*, 1920, **39**, 350). It is, however, evident that, although the use of invert sugar had previously been suggested, Gilmour had made the discovery independently, was the first to work it out fully in practice, and was, therefore, justified in claiming to be the first to show the effectiveness and cheapness of invert sugar as a reagent in the titration of boric acid.

Various attempts have been made to estimate boron compounds electrometrically. Mellon and Morris (*Proc. Indiana Acad. Sci.*, 1924, **35**, 85), found that boric acid could not be satisfactorily determined by this means in presence of polyphenols and organic acids. Van Liempt (*Rec. Trav. Chim.*, 1920, **39**, 358), however, found that electrometric determination of boric acid was possible under certain conditions.

To facilitate the titration of boric acid, certain other modifications have been suggested. Alcoholic sodium ethoxide is recommended for the titration of boric acid solutions in the presence of glycerol; the interfering action of carbon dioxide thus being eliminated. Barium hydroxide was also used by some investigators (J. Boeseken and H. Couvert, *Rec. Trav. Chim.*, 1921, **40**, 354). The interference of phosphoric acid can be prevented by the addition of sodium citrate (Kolthoff, *Chem. Weekblad*, 1922, **19**, 449). After neutralisation, addition of mannitol allows of the titration of the boric acid by further addition of sodium hydroxide. Neither calcium nor magnesium salts interfere. W. W. Deerns (*Chem. Weekblad*, 1922, **19**, 480) determined boric acid in presence of phosphoric acid by means of potassium iodide-iodate. The citrate method is not new, having been proposed by Littman (*Chem. Ztg.*, 1898, **22**, 691) and by Pfyl (*Arb. Kais. Gesund. Amt.*, 1914, **47**, 1).

BORIC ACID IN MILK.—In estimating boric acid in milk by Thomson's method, Liverseege and Bagnall (*ANALYST*, 1924, **49**, 133) found that, in presence of excess

of alkali, boric acid is not volatile at a red heat. This appears to suggest that so long as the percentage of fat in the substance is below a certain figure, no appreciable loss will result in the process of ignition. In the method detailed (ANALYST, 1923, 48, 416), the possibility of loss through ignition of fats and oils is overcome by extracting the fat with ether and igniting the defatted residue. I have found by experience that the fat portion extracted with ether contains a considerable amount of boric acid, so that it is always necessary carefully to re-extract the boric acid from the mixture of fat and ether by means of an aqueous solution of caustic soda and to add the latter to the bulk used in the determination.

SUMMARY.—From the foregoing historical notes it will be observed that the determination of boron compounds has passed through several interesting phases. In dealing with animal and vegetable products, the boron compounds can only be determined after all likely sources of interference have been eliminated or rendered inactive. Only in the case of a few definite classes of substances, such as butter and margarine, can actual separation of the organic matter, etc., be dispensed with, and a comprehensive method of general application, such as that already mentioned (ANALYST, 1923, 48, 416), is necessarily somewhat laborious. The main points to be observed in determining boron compounds in organic compounds are as follows:

- (1) Separation of the boron compounds from the organic matter.
- (2) Eliminating phosphates and carbonic acid, and
- (3) Choice of suitable indicators and media for the titration.

The first of these has for long been a source of worry to chemists; yet, curiously enough, it has hitherto not been very fully investigated. The present investigation was therefore carried out with a view to discover *inter alia* how the separation of boron compounds from the organic matter in animal and vegetable products can most readily be accomplished.

(To be continued.)

A New Reagent for the Colorimetric Determination of Minute Amounts of Copper.

BY THOMAS CALLAN, M.Sc., Ph.D., F.I.C., AND
J. A. RUSSELL HENDERSON, D.Sc.

THE literature dealing with the colorimetric determination of copper in water, foodstuffs and allied materials is a large one. Yoe (*Photometric Chemical Analysis*, Part I.—*Colorimetry*) gives a bibliography of some sixty references covering the years 1866 to 1926. Numerous reagents have been suggested for this determination, but the two which appear to have found most favour are potassium ferrocyanide and sodium ethyl xanthate, which give a pink and a yellow colour respectively with

copper. While the xanthate method is more sensitive than the ferrocyanide, the yellow colour is not a particularly good one for matching purposes, especially when the amount of copper is very small.

Quite recently Clarke and Jones (ANALYST, 1929, 54, 333) have put forward a method in which dimethylglyoxime is used in the presence of an oxidising agent. We find, however, that, whilst this method gives very good results, provided the conditions laid down by the authors are strictly adhered to, slight variations in the hydrogen ion concentration of the solution under examination have a marked effect on the intensity of the colour. Despite, therefore, the numerous reagents which have been put forward, a really satisfactory reagent still remains to be discovered.

Some time ago we found that sodium diethyldithiocarbamate,* $(C_2H_5)_2N.CSSNa$, which is a white crystalline substance readily soluble in water, and to a less extent in alcohol, and which is easily prepared by the action of carbon disulphide on diethylamine in the presence of alkali, gives a brown precipitate of the normal copper salt of diethyldithiocarbamic acid with solutions containing copper, and appeared to have distinct possibilities as a reagent for the determination of minute amounts of copper. This reaction has therefore been fully investigated.

The following table shows the results obtained with the new reagent (0.1 per cent. aqueous solution), compared with potassium ferrocyanide and sodium ethyl xanthate, with solutions of copper salts containing from 0.1 to 1 part per million of copper.

TABLE I.

Reagent.	1. 100 ml. distilled water.	2. 0.00001 grm. Cu in 100 ml. = 0.1 pt/million.	3. 0.00002 grm. Cu in 100 ml. = 0.2 pt/million.	4. 0.00005 grm. Cu in 100 ml. = 0.5 pt/million.	5. 0.0001 grm. Cu in 100 ml. = 1 pt/million.
Potassium ferrocyanide.	Slight darkening due to ferrocyanide.	Slightly deeper than 1 but no pink colour.	Slightly deeper than 2. Very faint pink colour.	Definitely pink in colour.	Considerably deeper in colour than 4.
Sodium ethyl xanthate.	No change.	Very slightly yellow.	Slightly deeper than 2. Yellow colour quite definite.	Proportional increase in depth of yellow colour.	
Sodium diethyl dithiocarbamate.	No change.	Very definite golden brown colour.	Deeper golden brown.	Still deeper golden brown.	Slightly cloudy and very deep golden brown colour. Appears to be about the upper limit to which it is desirable to go.

These results show (1) that sodium diethyldithiocarbamate is a more sensitive reagent than either potassium ferrocyanide or sodium ethyl xanthate, and (2) that the gradation in depth of colour with increasing amounts of copper is excellent.

We have found that the colour given with the new reagent is easily matched against the colours given by known copper standards, and that as little as one part

* Obtainable from British Drug Houses, Ltd., Graham St., City Road, London, N.1.

of copper per 100 million parts of distilled water gives a very faint colour, whilst the colour with one part per 50 million is quite definite.

The colour which the new reagent gives with copper is the same in neutral, acid or alkaline solution; cyanides inhibit the reaction, owing to the formation of a cuprocyanide which does not give the reactions for copper ions.

The reactions of sodium diethyldithiocarbamate with the more common metals have been investigated, and the results are given in Table II, where Column A gives the result of adding a concentrated solution of sodium diethyldithiocarbamate (about 20 per cent.) to a fairly strong solution of the metallic salt (5–10 per cent.), whilst column B shows the result of adding a 0.1 per cent. solution of the dithiocarbamate to dilute solutions of the metallic salts containing about 1 to 20 parts per million of the metal.

TABLE II.

	A.	B.
Aluminium	White curdy ppt.	White opalescence
Antimony	Yellowish white ppt.	White turbidity
Barium	Slight white ppt.	Clear
Bismuth	White curdy ppt.	White turbidity
Cadmium	Creamy white ppt.	White turbidity
Calcium	Slight white ppt.	Clear
Chromium	Dark green ppt.	Very faint turbidity
Cobalt	Greenish brown ppt.	Yellow coloration
Iron (ferrous)	Light brown ppt.	Brown colour
Iron (ferric)	Very dark brown ppt.	Deep brown colour
Lead	White curdy ppt.	White turbidity
Magnesium	Slight white ppt.	Clear
Manganese	Dirty yellow ppt.	Very faint turbidity
Mercury(ous)	White ppt.	Very faint turbidity
Mercury(ic)	Yellowish white ppt.	White turbidity
Nickel	Yellow green ppt.	Yellow white turbidity
Silver	Pale yellow ppt.	Very faint turbidity
Tin (stannous)	Buff ppt.	White turbidity
Tin (stannic)	Pale buff ppt.	—
Titanium	Dirty yellowish ppt.	Yellowish white turbidity
Uranium	Bright orange ppt.	Golden yellow colour
Zinc	White curdy ppt.	White turbidity

The effects of iron, lead and zinc on the copper reaction have been more fully investigated.

A. IRON.—Iron gives a brown colour which interferes with the copper colour. Iron, however, can be completely removed without loss of copper by adding excess of ammonia to the solution and filtering off the ferric hydroxide, the copper being determined in the filtrate.

B. LEAD.—Lead, if present in appreciable amount, gives a white turbidity in dilute neutral, acid or ammoniacal solution, the turbidity interfering with the copper reaction. If, however, a few drops of 10 per cent. ferric chloride solution are added to the lead-copper solution, and the solution boiled, made ammoniacal, and the precipitate filtered off, the whole of the lead is removed without loss of copper, which can then be determined in the filtrate.

C. ZINC.—Zinc in neutral solution gives a white turbidity. When, however, the zinc present does not exceed 0.1 grm. per 100 ml. (that is, 1000 times the maximum

amount of copper for which the method is applicable) the addition of 2–5 ml. of 0.880 ammonia per 100 ml. prevents its interference with the copper reaction, provided that the amount of reagent recommended is not largely exceeded.

METHOD OF DETERMINATION.—The following procedure has been found to be generally applicable:—The solution containing copper, freed from other metals when necessary, is made up to a suitable volume in a measuring flask, and an aliquot portion is pipetted into a 100 ml. Nessler cylinder, diluted with water, made slightly ammoniacal (or strongly ammoniacal if zinc is present), 10 ml. of a 0.1 per cent. solution of the reagent added, and the whole diluted to 100 ml. and well mixed.

Standard comparison solutions are prepared in the same way with suitable volumes of a copper solution containing 0.00001 gm. of copper per ml. This copper solution is prepared by dissolving 0.3928 gm. of pure recrystallised copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in a litre of water (1 ml. = 0.0001 gm. of copper), and further diluting 25 ml. of this solution to 250 ml. in a measuring flask (1 ml. = 0.00001 gm. copper). The amount of copper in the solution to be tested should not exceed 0.0001 gm. per 100 ml. (10 ml. of standard copper solution), as above this concentration the depth of colour becomes too dark for satisfactory matching.

The colour is quite stable for at least an hour, even when copper is present much in excess of the limit at which matching is possible, thus affording ample time for matching colorimetrically against standard copper solutions, but after this time a cloudiness develops, owing to the oxidation of the reagent.

An aqueous solution of sodium diethyldithiocarbamate keeps fairly well, a 0.1 per cent. solution in an amber-coloured bottle remaining apparently unchanged after several weeks.

An extended use of the reagent over a considerable period has confirmed its value and superiority over the more usual reagents. It was found to be of particular value in the course of a prolonged investigation of methods for the determination of copper in dyestuffs and rubber-proofed fabrics—a matter of no little importance in the rubber industry—and also in the determination of minute amounts of copper in acids, alkalis, etc.

We are indebted to Mr. H. E. Jones, of Messrs. Brunner, Mond & Co., Ltd., who has applied the new reagent to the determination of minute quantities of copper in caustic soda, for the following list of results, obtained in each case on 5 grms. of material:

SAMPLE A.		SAMPLE B.		
Copper added.	Copper found.	Copper added.	Copper found.	Added copper found.
Grm.	Grm.	Grm.	Grm.	Grm.
Nil	Nil	Nil	0.00014	—
0.00001	0.000008	Nil	0.00015	—
0.00002	0.000019	0.00007	0.00022	0.00007
0.00003	0.000029	*0.00015	0.00029	0.00014
0.00004	0.000040	*0.00010	0.00025	0.00010
0.00005	0.000049	*0.00015	0.00030	0.00015

In the cases marked * the amount of copper added was unknown to the analyst who made the determination.

In conclusion, we have to thank the British Dyestuffs Corporation, Ltd., in whose Central Analytical Laboratory the work was carried out, for their kind permission to publish the results of this investigation.

The Electrolytic Separation of Lead and Bismuth with Controlled Potential.

By ELLA M. COLLIN, B.Sc., A.I.C.

IN the methods hitherto described for the purely electrolytic separation of lead and bismuth (H. Sand, *J. Chem. Soc.*, 1907, **91**, 385; Lassieur, *Electroanalyse Rapide*, Paris, 1927, p. 108) the bismuth is first deposited at a controlled cathode potential, a reducing agent being added to the solution, and the lead is then deposited as metal. The reducing agents used by Sand were glucose and tartaric acid, but Lassieur substituted hydroxylamine hydrochloride. The deposition of lead as metal on the cathode is not free from objections, owing to its great tendency to oxidation on drying, and also to its deleterious effect on the platinum electrode.

The method given here is a modification of that given by Sand (*loc. cit.*), hydrazine hydrate being used as the reducing agent. This has the great advantage that it is easily destroyed, thus enabling the lead to be deposited as peroxide on the anode after the separation of the bismuth.

It is well known that, owing to the tenacity with which water is retained by lead peroxide, an empirical factor, which depends to some extent on the conditions of deposition and drying, must be employed for the calculation of PbO_2 to Pb. (H. Sand, *Chem. News*, 1909, **100**, 269; R. O. Smith, *J. Amer. Chem. Soc.*, 1905, **27**, 1287; A. Fischer, *Z. Elektrochem.*, 1904, **10**, 945.) Several experiments were carried out with a view to finding such a factor for the amount of lead deposited as peroxide.

All the experimental work in this paper was done with a rotating electrode, and with the use of the apparatus designed by Sand and described by him (ANALYST, 1929, 275).

The solution, containing the lead as nitrate, is treated with a strong solution (about 50 per cent.) of sodium hydroxide, just sufficient to redissolve the precipitate, and then acidified with nitric acid, 20 c.c. in excess being added; the total volume is about 120 c.c. It is electrolysed at a temperature of $90^\circ\text{--}95^\circ\text{C.}$, with a current of $6\text{--}6\frac{1}{2}$ amps. In each experiment, before disconnecting, a small quantity of the solution is withdrawn, made alkaline, and tested with hydrogen sulphide, to ensure that the deposition of the lead is complete. The deposit is dried by dipping the electrode in alcohol and then ether and holding it at some distance above a Bunsen flame.

Amount of lead taken. Grm.	Weight of PbO_2 found. Grm.	Factor $\text{PbO}_2:\text{Pb}$.
0.1000	0.1153	0.8673
0.1000	0.1156	0.8651
0.2000	0.2318	0.8628
0.3000	0.3467	0.8653
0.4030	0.4640	0.8620
0.5072	0.5895	0.8604

On the basis of these results the factors taken for the calculation of PbO_2 to Pb in the subsequent determinations are as follows:

Up to 0.1 gm. Pb	0.8660
From 0.1 gm. Pb to 0.4 gm. ..	0.8635
From 0.4 gm. Pb to 0.5 gm. ..	0.8605

These factors agree closely with those found by Sand, Smith and Fischer.

THE SEPARATION OF LEAD AND BISMUTH.—To the solution of the two metals, present as nitrates in a volume of about 60 c.c., is added an excess of 3 c.c. of nitric acid, and 4 or 5 drops of a 50 per cent. solution of hydrazine hydrate. The electrolytic deposition of the bismuth is carried out at a temperature of 80° – 85° C., according to the method described by Sand (*J. Chem. Soc.*, 1907, 91, 373), but with a *N*/100 nitric acid quinhydrone auxiliary electrode, the initial current being 1.3 amps. at a cathode potential of -0.45 volt (referred to the quinhydrone electrode), which is reduced by the end of the electrolysis to practically zero at a potential of -0.6 volt. After the removal of the bismuth a strong solution (about 50 per cent.) of caustic soda is added to the electrolyte while it is still hot, until the precipitated lead hydroxide is just redissolved. Sodium peroxide is then added in small quantities, and the solution heated until all brown fumes and precipitate have cleared. The addition of the sodium peroxide is continued until the last portion produces no further brown fumes. The solution is heated gently for about five minutes, and then cooled somewhat. It is then acidified with concentrated nitric acid, with the addition of 20 c.c. in excess, the total volume by this time being about 120 c.c. The solution is electrolysed, as previously described, with a current of 6–6.5 amps.

RESULTS.

Taken.		Found.	Time taken for electrolysis.
Grm.	PbO_2 Grm.	Grm.	Minutes.
Bi: 0.1000		Bi: 0.0997	7
Pb: 0.4000	0.4627	Pb: 0.3995	12
Bi: 0.3882		Bi: 0.3875	12
Pb: 0.2000	0.2313	Pb: 0.1997	15
Bi: 0.2103		Bi: 0.2105	10
Pb: 0.4325	0.5005	Pb: 0.4322	18
Bi: 0.2000		Bi: 0.1996	10
Pb: 0.2000	0.2305	Pb: 0.1990	12
(Trace of lead found in electrolyte.)			
Bi: 0.1000		Bi: 0.0998	8
Pb: 0.1000	0.1155	Pb: 0.1000	12
Bi: 0.4000		Bi: 0.4010	15
Pb: 0.4000	0.4622	Pb: 0.3991	15

In conclusion, I wish to express my thanks to Dr. H. Sand for his suggestions and interest during the course of this work.

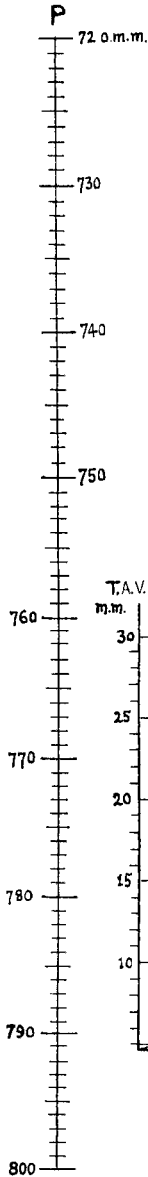
THE SIR JOHN CASS TECHNICAL INSTITUTE,
LONDON, E.C.3.

A Nomogram for Converting Observed Volumes of Gas to Normal Temperature and Pressure.

By J. H. COSTE, F.I.C.

(Demonstrated at the Meeting, October 2, 1929.)

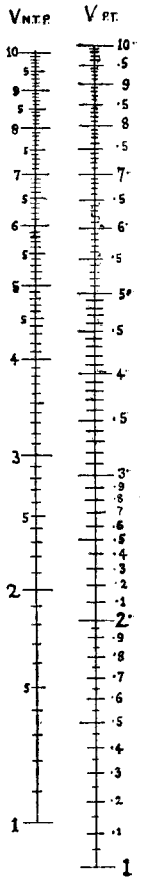
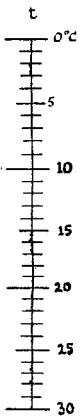
$\frac{P}{T}$



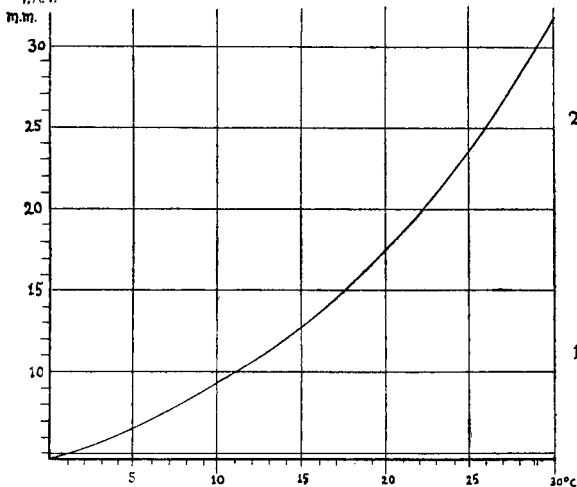
NOMOGRAM for reducing VOLUMES of GAS to N.T.P.

TO USE: Note where line passing through points on lines P and t, representing observed Pressure and temperature, cuts line $\frac{P}{T}$. The corrected volume at N.T.P. is read on line $V_{N.T.P.}$ where line from point on $\frac{P}{T}$ to observed volume on line V_{pt} cuts it.

N.B. - P is actual pressure. If gas is wet subtract T.A.V. (see below) from P. obs.



T.A.V.
m.m.



THE attached nomogram has been drawn to enable necessary corrections to standard temperature and pressure to be made over a reasonable range of variations of temperature and pressure with sufficient accuracy for many purposes.

The four graduated lines, P, t, V_{pt} and V_{NTP} , represent the logarithms of the natural numbers inscribed against them, and are placed at such distances apart as are appropriate to the scales. The manner of using the nomogram is inscribed thereon. Exact alignment on the scales and pivoting on the ungraduated line, P/T, is best secured by cutting a strip of transparent celluloid with a V-notch at one end and a line drawn with a point (a gramophone needle is convenient) along from the point of the V to the other end of the strip. This can be aligned on the relevant points on P and t and slid along until a pin held in the point of the V-notch touches P/t, in which it is stuck. The scratched line of the slip can then be brought to coincide with the observed volume on V_{pt} and the corrected volume read off on V_{NTP} .

Examples:—

- I. 8.31 c.c. of gas at 17° and 730 mm. (dry) = 7.48 c.c. at N.T.P. (Five figure logarithms give 7.51 c.c.)
- II. 11.3 c.c. of gas at 4° and 777 mm. (moist) = 11.3 c.c. at N.T.P. (Five figure logarithms give 11.30 c.c.)

This nomogram has been in use for some years. I notice that one has recently been described by O. Liesche (*Chem. Fabr.*, 1928, 583-4, 595-7, 621-3).

DISCUSSION.

Mr. G. N. HUNTLY stated that he had found Dr. Farmer's gas calculator* for reducing gas volumes very useful. This gave, not the corrected volume, but the factor for reducing to N.T.P. by a single multiplication. Its accuracy was 1 in 5000.

* Published by Baird & Tatlock (London) Ltd.

Official Appointments.

THE Minister of Health has confirmed the following appointments:

MR. A. E. JOHNSON, B.Sc., F.I.C., as Public Analyst for the County Borough of Wolverhampton, to date from December 10, 1929; also as Public Analyst for Newcastle-under-Lyme, to date from December 1, 1929. Mr. E. Victor Jones, F.I.C., relinquishes these appointments on the respective dates mentioned.

MR. D. T. LUCKE, B.Sc., A.I.C., as Additional Public Analyst for the County Borough of Southend-on-Sea.

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.

ROUTINE DETERMINATION OF SALT IN BUTTER AND MARGARINE.

THE method published by Steuart (ANALYST, 1928, 53, 212) was examined and found to be amenable to further simplification by the use of 10 c.c. of hot water instead of acetone. The following method is proposed for rapid routine determinations:—Weigh 3 grms. of the sample on a large cigarette paper, and drop paper and sample into a 150 c.c. conical flask. Add 10 c.c. of boiling distilled water, shake well, and titrate with 0.1 N silver nitrate solution, using chromate indicator; towards the end-point, close the flask and shake well, as in Steuart's method.

This method gives results which are the same as those obtained by the acetone method, and are in substantial agreement with results obtained by the standard method, consisting in drying the butter or margarine, extracting the fat with petroleum spirit, extracting the solids-not-fat with water, and filtering and titrating the aqueous extract as usual. The following results will give an idea of the agreement obtained, and it will be seen that the differences are not of such an order as to play any part in the commercial judgment of butter or margarine:

Sample No.	Salt by standard method.	Salt by rapid hot water method.
	Per Cent.	Per Cent.
1	4.80	4.58
2	2.59	2.65
3	2.20	2.04
4	1.63	1.67
5	1.42	1.46
6	0.95	0.92
7	0.59	0.65
8	0.31	0.37

PAUL ARUP.

BUTTER TESTING STATION,
DUBLIN.

EXAMINATION OF GOATS' MILK FOR UNBOILED MILK.

IN testing whether the goats' milk sold in Gibraltar complies with the Regulation that it shall have been boiled (*cf.* ANALYST, 1929, 593) the following method of estimating small amounts of unboiled milk is used. The milk should be fresh, and it is not practicable to estimate more than 30 per cent. of unboiled milk; when there is more than this the results are returned as indicating wholly unboiled milk.

The colorations given by the enzymes in milk (which are destroyed on heating

the milk to 80° C.) with various reagents in the presence of hydrogen peroxide are as follows:—Ortol, deep red; paradiaminobenzene, indigo-violet; hydroquinone, deep pink; guaiacol, brick red; guaiacum, blue. The results of tests which I made indicated that ortol is the most sensitive of these reagents, with paradiaminobenzene next. With either of these as little as 2·5 per cent. of unboiled milk could be detected with certainty, but with guaiacol 30 per cent. could escape detection.

ORTOL METHOD.—The test is as follows:—Place 5 c.c. of the milk in a test tube, and add 1 drop of 10 per cent. hydrogen peroxide (90 vol.), and then 1 c.c. of a freshly made 1 per cent. aqueous solution of ortol. (If less than 10 per cent. of unboiled milk is to be estimated, the hydrogen peroxide is reduced to 2 drops of a 1 per cent. solution.)

The colour is formed almost at once if unboiled milk is present, whereas for wholly boiled milk only a slight pink is discernible after some time. In the presence of 2·5 per cent. of unboiled milk the pinkish colour is formed at once.

The colour formed is compared with those obtained with known percentages of unboiled milk, standards and tests being made at the same time.

The Paradiaminobenzene method, which I use as a confirmatory test, is carried out in a similar manner, the strengths used being as follows:—Paradiaminobenzene, 0·25 per cent. aqueous solution; hydrogen peroxide, 1 drop (90 vol. equally diluted); milk, 5 c.c. Readings should be taken after one minute and not later than two minutes after mixing. Wholly boiled milk develops a bluish tint from three to five minutes.

I was driven to make these experiments because the Pasteur Institute at Tangier differed from my findings of 10 per cent. of unboiled milk in a prosecution case last year. The Pasteur Institute used guaiacol, which, as I found experimentally, does not detect 30 per cent., or even more, of unboiled milk.

A. G. HOLBOROW.

CITY COUNCIL LABORATORIES,
GIBRALTAR.

DISTRIBUTION OF ARSENIC IN THE BODY IN A FATAL CASE OF POISONING BY HYDROGEN ARSENIDE.

IN connection with a fatal case of arsenical poisoning which occurred in Westland, New Zealand, in 1926, it became necessary, owing to legal issues involved, to investigate the cause of death more fully than usual. As the distribution of arsenic in the body in cases of gaseous arsenical poisoning appears to have been recorded on comparatively few occasions, a brief account of this case should be of interest.

The liberation of hydrogen arsenide resulted from the treatment of zinc slimes by sulphuric acid during the recovery of gold by the cyanide process. No special precautions were taken to carry off the gases evolved during the process, and the conditions were such that it was probable that gases evolved would be inhaled by the operator. The plant had been in operation for a considerable time, when the operator was suddenly taken ill. Two days later he obtained medical advice, when arsenical or similar poisoning was diagnosed. Treatment on these lines was given, but death occurred after 9 days, the immediate cause of death being complete suppression of the urine.

The organs referred to below were submitted to me, as district Government Analyst, for chemical analysis, with a request for a full examination, as important issues were involved. Arsenic was detected by the Reinsch test, and quantitative

determinations were then made on fairly large amounts of each organ. Destruction of organic matter was effected by digestion with nitric and sulphuric acids, the former being added in small quantities till the liquid ceased to char (modified Gautier's process). The liquid, freed from nitric acid by further heating, was then suitably diluted. The arsenic present was determined by the electrolytic Marsh process, with the use of a platinum anode and a lead cathode (see Sand and Hackford, *J. Chem. Soc.*, 1904, 58, 1018; and Monier-Williams, *ANALYST*, 1923, 48, 112, 262).

Blank determinations with the reagents used gave negative results. The distribution of arsenic was as under:

Organ.					Arsenic present (calculated as As). Mgrms. per kilo.
Brain	1.40; 1.0
Lungs	2.59; 2.3
Stomach and contents			0.10; 0.3
Spleen	0.48; 2.2
Kidney	0.36; 1.3
Liver	6.90; 4.4.

I expressed the opinion that the distribution would be consistent with gaseous arsenical poisoning, and a verdict was given on these lines.

At the time of the accident roasted concentrates were being treated, and an unusual white precipitate had been observed in the zinc precipitating boxes, which the operator thought was cyanide of zinc. Subsequent to the accident an investigation was made by the company, and it was found that the roasted concentrates contained 1.4 per cent. of arsenic (calculated as element). The white precipitate in the boxes contained 8.0 per cent. of arsenic (element), also lime and zinc. The percentages of lime and zinc, and the nature of the combination, whether arsenate or arsenite, were not determined. A white deposit, similar in appearance, which had collected in the pipe leading from the cyaniding tank to the zinc boxes, consisted almost entirely of carbonate and arsenate of lime, the percentage of arsenic present (calculated as element) being 9.85. The lime in both precipitates had, no doubt, been derived from lime used to counteract possible acidity of the concentrates. It was found that hydrogen arsenide was evolved when these precipitates were treated with sulphuric acid in the presence of zinc. The presence of hydrogen arsenide being accounted for, no further chemical investigation was carried out by the company.

The danger attached to the process was successfully overcome by the provision of adequate means of removing the evolved gases from the sulphuric acid vat. The vat was closely covered, and the gases conveyed to a flue by a current of compressed air. Hydrochloric acid was eventually substituted for sulphuric acid, thus avoiding the necessity for stirring.

I wish to thank Dr. J. S. Maclaurin, Dominion Analyst, Wellington, for permission to publish these results.

F. J. T. GRIGG.

GOVERNMENT LABORATORY,
CHRISTCHURCH, NEW ZEALAND.

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 AND COUNTY OF KINGSTON-UPON-HULL.

ANNUAL REPORT OF THE PUBLIC ANALYST AND BACTERIOLOGIST FOR THE YEAR 1928.

DURING the year the number of samples and specimens examined was 7479. Of these, 1666 were food and drugs samples, comprising 808 official, 427 informal, and 431 miscellaneous samples; 74 of these were suspicious, and 54 (3·8 per cent.) were adulterated. The lower percentage of adulterated and suspicious samples, as compared with the year 1927, was largely due to the more definite position regarding the illegality or otherwise of the use of preservatives.

DIRT IN MILK.—Only 6 of the 579 samples of milk examined contained unwarranted amounts of dirty sediment; this is the lowest figure recorded for some years.

BONDON CHEESE.—A sample of so-called *Bondon Cheese* was reported as adulterated, since it was a skimmed-milk cheese containing only 5·3 per cent. of fat. The opinions of traders as to the method of manufacture and the composition of this cheese are conflicting, but it can scarcely be denied that Neufchâtel Bondon Cheese was originally made, and is to-day made, from whole milk. Therefore such cheese should be prepared as in Neufchâtel, France, and should contain at least 20 to 25 per cent. of fat.

ICE-CREAM.—Twenty samples were examined chemically during the year, and all were found to consist of sweetened farinaceous mixtures, with milk or milk and water as a basis. The amount of milk-fat present in the samples varied from 1·0 to 4·4 per cent., with an average of 2·5 per cent. No fewer than 14 out of the 20 samples contained less than 3·0 per cent. of fat, and nine less than 2·5 per cent. All the samples failed to approach the standard of 6 or 8 per cent. milk-fat suggested by the trade and other bodies. These confections were therefore not properly named "ice-cream," which term should certainly be restricted to a product containing some addition of cream to the milk (not milk and water) used in making them. All the 20 samples were free from preservatives and deleterious metallic contamination.

Twenty-nine samples were examined bacteriologically, and 13 were found to be more or less contaminated with objectionable organisms, due to unclean utensils and methods of manufacture. These 13 samples contained from 140,000 to 16,000,000 organisms per c.c., with evidence of the presence of the *Bacillus coli* in one-thousandth to one ten-thousandth of a cubic centimetre of the melted samples. Ice-cream of satisfactory purity ought to contain no *Bacillus coli* in less than 0·1 c.c. Inspections of the premises where ice-cream is manufactured have been made during the year by the sampling officer, and, where necessary, representations have been made to the owners regarding improved methods and plant.

COFFEE AND CHICORY EXTRACT (POWDER).—A sample of this new product had the characteristics to be expected in a dried extract, in powder or "scale"

form, of the soluble substances in coffee and chicory; it contained about 4 per cent. of caffeine. The label, however, was considered unsatisfactory, in that it did not specify the nature of the contents, but bore the words: "—Coffee. Sold as a mixture of Coffee and Chicory." On the attention of the manufacturers being called to the matter, they agreed to alter the wording to read: "A desiccated extract of Coffee and Chicory."

CONFECTIONERY (SWEETS).—Two of the 24 samples of cheap sweets (chocolates, candy, nougat, pastilles, etc.) purchased in the vicinity of the Fair Ground, contained 850 and 1640 parts per million of sulphur dioxide. Action was taken in connection with the second (formal) sample, and the vendor was fined £1.

MUSTARD AND PREPARED MUSTARD.—Ten samples of mustard and 5 of prepared mustard were examined during the year. Of the 10 mustard samples, 6 were genuine, while 2 contained a farinaceous addition; in one sample 20 per cent. of wheat-flour, and in the other 10 per cent. of maize-flour (cornflour). These were also regarded as genuine, since each was labelled as a "mustard compound," and sold as a mixed article. Two other samples (adulterated and of suspicious character) contained 2 per cent. of maize-flour, with turmeric.

The five samples of *prepared mustard* are the first to be examined in the City Laboratory. These preparations, frequently known as "French" or "German" mustard, consist generally of mustard which has been mixed with vinegar and probably with water in addition, together with salt, and sometimes spices. Provided such articles contain a due amount of mustard—the main ingredient in a satisfactory preparation—and no "filling" ingredient without disclosure, they may be regarded as satisfactory in nature. Four of the 5 samples passed these requirements, and showed an average content of about 65 per cent. of water, including 1-4 per cent. of the acetic acid of vinegar. The remaining sample (an English preparation) showed evidence of an appreciable proportion of wheat flour. There was no disclosure by label in this instance, and the sample was reported as of suspicious character.

PEPPER AND PEPPER MIXTURES.—Nineteen samples of this condiment, many of them being sold in 1d. and 2d. cartons or tins, were examined. Seventeen of the samples were sold as pepper, and 3 of these were reported as of suspicious character; two contained about 1 per cent. of maize flour with turmeric colouring-matter, while the other sample contained the same amount of a mixture of maize-flour and arrowroot with added colouring matter. Fourteen samples consisted of the genuine ground spice, though some were coloured with turmeric. The two remaining samples were labelled "Prepared Pepper" and "Compound Pepper," and also bore the words on the containers, "Sold as a mixed article." Each consisted of equal weights of pepper and a foreign substance, in one instance rice-flour and in the other, maize-flour. The labels protected the vendors, though why it is supposed that the public likes these "fillings," which are useless in pepper, is difficult to understand. It is unsatisfactory that the word "pepper" in such cases is allowable in law.

ICE.—Ice used for putting into summer drinks should be bacteriologically pure, and should always be washed in clean water before use. Two samples of ice examined showed somewhat unsatisfactory results, since they contained four to eight thousand organisms per c.c. and *Bacillus coli* in 0.1 c.c. and in 1 c.c. Representations were made to the proprietors of the cafés concerned.

SHRIMPS.—Two samples of boiled shrimps, examined bacteriologically, proved to be free from organisms of the food-poisoning (*Salmonella*) group, and of the typhoid-paratyphoid group, but the *Bacillus coli communis* was present in one

sample to the extent of about 40 per fish, and these shrimps were regarded as unsatisfactory. A further sample from the same source proved to be of satisfactory purity.

SUNLIGHT (ULTRA-VIOLET RAYS) OBSERVATIONS.—These observations have been continued throughout the year, and, during most of this period, records have been taken at two stations. The central area was represented, as before, by an apparatus placed on the roof of the Telephone Exchange in Mytongate, while a suburban site was chosen in February at Pearson Park (roof of greenhouse). The “units of fading” of the standard coloured solution used are a measure of the ultra-violet rays in the sunlight reaching any given area. The maximum and minimum daily average figures for the two Hull stations, together with those of certain other towns, are given in the following table. The daily “units of fading” are calculated from the total of each separate month’s records:—

UNITS OF FADING. DAILY AVERAGE THROUGHOUT THE MONTHS MENTIONED.

	Maximum.	Minimum.		Maximum.	Minimum.
Hull (Central) ..	2·8 (July)	0·2 (Dec.)	London Kingsway	6·8 (July)	0·2 (Dec.)
„ (Suburban) ..	3·2 (July)	0·2 (Dec.)	„ Hampstead	15·8 (July)	0·5 (Dec.)
Cardiff ..	5·2 (July)	0·9 (Dec.)	Lowestoft ..	13·0 (Aug.)	1·5 (Jan.)
Huddersfield ..	3·9 (July)	0·3 (Jan.)	Stirling ..	3·4 (June)	0·5 (Jan.)

STAINED FABRIC.—A piece of white fabric, said to have been stained by boiling in water in a gas-boiler, was submitted for examination. The lining of these boilers has previously been shown to consist of an alloy of lead and tin, and the stains on the cloth contained a material amount of the first-named metal.

A. R. TANKARD.

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.

PEPPER COMPOUND.

ON August 20, a shopkeeper was summoned at Sheffield for selling a mixture which was not the pepper compound demanded.

An inspector had bought from the defendant’s shop cartons, labelled “Penny Pepper,” which were being sold as “Pepper Compound.” On analysis, the mixture was reported to consist of 50 per cent. of pure pepper and 50 per cent. of rice starch.

Mr. A. Neal, for the defence, said that the wholesale merchants would be prepared to justify their position if their warranty was accepted. Their invoice, bearing a guarantee that the goods were of the nature, substance and quality described, was produced.

The magistrates accepted the warranty and dismissed the case.

On October 16, the summons against the wholesale merchants who had given the warranty was heard.

Mr. W. A. Williams, for the prosecution, contended that the articles referred to in the warranty were not of the nature described. If a compound constituted

a fraud upon the public, the fact that it was described as a compound was no protection. The purchaser would imagine that he was getting something similar to pepper in that part of the compound which was not pepper.

Mr. John Evans, F.I.C., Public Analyst for Sheffield, who was called in support of his certificate, said that he had detected traces of other substances, such as pea meal and capsicum, in the compound, but that he had regarded them as mere impurities.

Mr. S. E. Melling, Public Analyst for the County of Cheshire, called in support of the City Analyst's Certificate, said that the amount of rice in the mixture was excessive, but agreed that he could not fix a standard.

Mr. F. W. Scorah, solicitor for the defence, submitted that the Bench had power to fix a standard on the evidence, and in that case they could not say that the amount of rice was excessive.

Mr. E. J. Parry, F.I.C., said that there was no legal standard for pepper compound. He accepted the evidence that there was 50 per cent. of rice-flour in the compound, but said that the rice-flour was impregnated with capsicine, which was 500 to 1000 times as pungent as pepper, and found other spice extracts. He considered that the compound had been prepared by the most reasonable method.

The Chairman of the Bench said that he did not understand why, when other substances had been detected, they were not mentioned in the Analyst's certificate. The Bench were of opinion that a case had not been made out, and dismissed the summons.

SULPHUR DIOXIDE IN GROUND GINGER.

ON September 25, a co-operative society was summoned at Eccleshall (Staffs.) for selling ground ginger containing 0.0416 per cent. of sulphur dioxide, and a Lancashire wholesale co-operative society was summoned for giving a false warranty in respect of this ginger.

For the defence it was stated that the ginger had been sold by the wholesale co-operative society, as received from their depôt in India, where there were no restrictions on the use of sulphur dioxide for ginger. The preservative was used to protect the ginger root from the effects of damp. The defendants undertook to do their best not to put any more such ginger on the market.

The case against the first defendants was dismissed, and the wholesale co-operative society was fined £3, with £5 1s. 6d. costs.

REMOVAL OF ORIGIN MARKS FROM EGGS. USE OF ULTRA-VIOLET RAYS IN COURT.

ON October 8, a tradesman was summoned at Glasgow for having sold, as fresh country eggs, imported eggs from which the mark of origin had been removed, the allegation being that an acid had been used for this purpose.

Mr. T. Cockburn, Chief Assistant in the Glasgow Corporation Laboratory, supplemented this evidence by making an actual demonstration in Court with an ultra-violet light apparatus. He showed how eggs could be examined by means of this apparatus, and demonstrated that the area of corrosion by acid showed a deep purple colour, as compared with the light colour of the remainder of the shell. He then placed under the rays the eggs which formed the subject of the summons.

The Stipendiary Magistrate said that he was satisfied that there had been tampering with the eggs, and imposed a fine of £5, with £3 costs.

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

FOR THE YEAR ENDING MARCH 31st, 1929.*

THE chemical work of the same Government Departments as in previous years was undertaken (ANALYST, 1928, 53, 593-596), and, in addition, work has been done in connection with the Ethyl Petrol Committee, the Atmospheric Pollution Research Committee and surveys of rivers. The total number of samples examined was 499,289, an increase over the previous year of 8250. The Hydrocarbon Oils Duty involved the examination of over 12,000 samples, and there is again an increase in tobaccos for payment of drawback on exportation (74,415 samples against 44,365) owing to the increased manufacture of cigarettes for export from duty-free leaf. The discontinuance of bonded sugar refineries accounts for an increase of about 7000 sugar samples. Wine and tea samples have decreased from 99,391 to 85,703, and 41,149 to 28,896 samples, respectively.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter*.—Five of 863 samples contained over 16 per cent. water, and 15 samples from one source had approximately 50 per cent. of foreign fat. *Margarine*.—Only 7 out of 341 contained excess water. *Cheese*.—Fifty per cent. of the samples were from cheeses prepared from whole milk, 23 from milk with three quarters to the whole of its fat, 10 from milk with half to three quarters fat, and 17 from milk with less fat. *Cream*.—Two samples of artificial cream were emulsions of whole milk and foreign fat. *Condensed milk*.—Fifteen samples of 62 were made from machine-skimmed milk, and not marked accordingly. *Sheep dips*.—Five of 67 samples were unsatisfactory.

Water and Pollution of Rivers.—Fifty-four samples of river-water, muds and effluents were examined. The diurnal variations in the quantity of dissolved oxygen in rivers have been further studied.

Fertilisers and Feeding Stuffs Act.—Of 6 fertilisers examined, one fertiliser and one superphosphate were deficient in soluble phosphoric acid, a basic slag was deficient in fine material, and 2 out of 3 shoddies in nitrogen. Of 15 feeding stuffs, 3 samples of barley meal each contained between 25 and 40 per cent. of foreign material from tapioca root and wheat offal, 2 samples contained 2.5 and 5.0 per cent. of oats, together with small quantities of wheat and weed-seeds; a sample of meat and bone meal was deficient in phosphates, and a sample of meat meal in oil; it also contained over 4 per cent. of salt. Two samples of meat and bone

* Obtainable at Adastral House, Kingsway, W.C.2. Price 1s. 6d. net.

meal were deficient in phosphoric acid. Two laying meals were deficient in oil and protein, and one had an excess of sand; a sample of fine offals contained, in addition, 20 per cent. foreign matter, and 2 samples of feeding cake were deficient in protein. There were 2 cases of disagreement with agricultural analysts, one relating to a deficiency of nitrogen in a shoddy, and the other of protein in a feeding cake.

Miscellaneous Articles.—Fifteen samples of barley and barley meal were examined as causing illness in pigs, 2 samples of crustless cheese, to ascertain the nature of the emulsifying substance, 8 samples of rat and beetle poison, etc.

CUSTOMS AND EXCISE.—*Beer.*—The total number of samples examined was 56,236, a decrease of 1715 over the previous year. Of these, 355 consisted of malt corn, brewing sugars, exhausted grain; 207 were yeast food or miscellaneous substances; 6917 samples were for checks on assessment of duty; 7052 for checking whether dilution of beer had taken place (262 samples showed dilution had taken place, and in 20 cases it amounted to over 4 gallons of water per barrel). Tests for arsenic were made on 1238 samples, and 39 of these contained arsenic in slight excess of that allowed by the regulations. *Cider.*—Thirty-six samples of imported cider out of 188 were found to be dutiable. *Cocoa and chocolate.*—Examinations of 9501 samples from imported goods and 3425 from exported goods were made to ascertain the proportion of various ingredients present in connection with duty. *Dangerous Drugs Act.*—Six of 49 suspected drug samples contravened the Act.

Hydrocarbon Oils Duty.—The 1928 Finance Act defines "Light Oils" as "hydrocarbon oils of which not less than 50 per cent. by volume distils at a temperature not exceeding 185° C., or of which not less than 95 per cent. by volume distils at a temperature not exceeding 240° C., or which give off inflammable vapour at a temperature of less than 22·8° C. when tested in the manner prescribed by the Acts relating to petroleum." For the new duty purposes 12,055 samples were examined between 25th April, 1928, and 31st March, 1929, 9748 from imported and 2307 from exported goods. Of these, 3410 were hydrocarbon oils and 8645 goods such as enamels, lacquers, road dressings, insecticides, essential oils, etc.

Safeguarding of Industries Act.—In order to find whether the chemical was liable to duty, or whether substances bearing trade names contained dutiable ingredients, 12,288 samples were examined. *Silk.*—In connection with duty 20,872 samples were examined, 10,368 from imports, 9578 from exports, and 926 from home factories. *Spirits.*—Wood and mineral naphtha (606), pyridine (127), special denaturants (1537), exported spirits for drawback claims (2510), exported spirituous preparations (18,771) and imported spirits and spirituous preparations (13,724) were examined. *Sugar, glucose and saccharin.*—Of sugar and articles containing sugar or other sweetening matter, 68,935 samples were examined for duty or drawback assessment. *Table Water Duty.*—Of 26 mineral waters, 5 were medicinal, and 21 liable to table water duty. *Tea.*—Of 28,896 samples of tea 298 were reported against, 187 on account of foreign substances and 111 as being unfit for human consumption. *Tobacco.*—The largest number of samples are in connection with manufactured tobacco and commercial snuff for exportation on drawback; 74,415 such samples were examined, particularly for moisture, and in the case of cigarettes for paper. Offal tobaccos for repayment of duty involved examination of 42,710 samples, 29,133 of stalks, and 10,960 of offal snuff, shorts and smalls.

MINISTRY OF HEALTH.—*Preservatives Regulations.*—Examination for presence of preservatives, which are only allowed in a few specified articles to limited extent,

was carried out on 2529 samples, and 44 were reported to the Board of Customs and Excise as contravening Regulations. These included 17 samples containing sulphur dioxide either contrary to the Regulations or in excess of permitted quantities; 9 samples of tinned vegetables containing copper colouring matter; boric acid in a sample of bacon, salicylic acid in 2 fruit juices, and hydrogen peroxide in one, and boron preservative in 12 butters; no boric acid was found in margarine samples.

HOME OFFICE.—The total number of samples was 527. The yellow colour of a sample of shellac was found to be derived from added sulphide of arsenic.

FOOD AND DRUGS ACT.—Of the 27 samples of food referred under the Acts, 17 were milks, 4 butters alleged to contain foreign fat, gin and whisky with excess of water, rice with excess of mineral glaze, and ginger wine, ginger beer, and raspberry cordial containing salicylic acid. A calomel ointment was deficient in calomel, and an ammoniacal tincture of quinine in quinine. There were 4 cases of disagreement with the prosecution's analyses. Three samples of butter did not afford evidence of the presence of fat other than butter fat, and a milk alleged to be deficient in non-fatty solids contained 8.61 per cent.

D. G. H.

Medical Research Council.

TOXICITY TESTS FOR NOVARSENO BENZENE (NEOSALVARSAN).*

THE test necessary for novarsenobenzene must ensure that its toxicity does not exceed that of a standard by more than a specified amount. At present the British test is not sharply definitive, allowing an undue proportion of toxic samples to pass, the German is rather sharper, and the Japanese and American less discriminative. The proposed improved test is as follows:—The drug is dissolved in freshly re-distilled water to give a 2 per cent. solution, and the fresh solution is injected into the tail veins of the mice, which are made to fast over-night, weighed, and then given food, and the injection made 1 hour later. In the first stage 10 animals weighing 18–20 grms. are injected with 7.6 mgrm. each of the novarsenobenzene. If not more than 2 die (20 per cent. mortality) the sample is passed, and among those passing would be samples with a toxicity less than that of the standard and about 61 per cent. of those with a toxicity equal to that of the standard. The others are injected in the same dose into a further 10 mice, and the total mortality on the 20 animals so far used observed, and, if not over 40 per cent., the sample passes. A further 38 per cent. of samples of standard toxicity should pass. If more than 15 animals have been killed, the sample is rejected as exceeding the permissible toxicity. The remaining samples are injected into a further 10 mice, and those which have not killed more than 15 of the total 30 are passed and the rest rejected, so that 50 per cent. of 30 mice on a dose of 0.4 mgrm. must survive.

The test passes all samples of toxicity up to that of the standard, rejects 0.4 per cent. of those of toxicity 10 per cent. over the sample, 50 per cent. of those 20 per cent. above, and 99.6 per cent. of those 30 per cent. above. With a dose of

* Special Report No. 128, by E. H. Durham, J. H. Gaddum and J. E. Marchal. Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 9d. net.

0.38 mgrm., or a total dose of 7.2 mgrm., 94 per cent. of the samples 30 per cent. above the standard toxicity pass, and 11 per cent. of those 30 per cent. above.

The sensitiveness of the stock of mice is tested from time to time by means of the standard, so that comparable results may be obtained by workers in different laboratories.

D. G. H.

Sandstone Industry (Silicosis) Scheme, 1929.

UNDER the Workmen's Compensation (Silicosis) Act, 1928 (8 & 9, Geo. 5) the proprietors of stone quarries and firms dealing with sandstone or similar material containing more than 50 per cent. of silica (free or combined) must insure against liabilities in connection with silicosis under the Act. The following Statutory Rules and Orders made under the Act deal with the question of silicosis:—No. 12, 1919; No. 41, 1924; No. 79, 1925; No. 975, 1928; No. 171, 1929.

For the purposes of this Scheme "sandstone" includes ganister, gritstone and quartzite rocks, but does not include rotten-stone or natural sand.

Paragraph 2 (3) (11) of the Sandstone Industry (Silicosis) Scheme, 1929, provides that: "Where an employer satisfies the Secretary of State by chemical analysis carried out in accordance with such conditions as may be prescribed that the sandstone got or manipulated at any mine, quarry or other premises does not contain more than 50 per cent. silica (free and combined), the Scheme shall, as from such date as may be specified by the Secretary of State, cease to apply to any processes carried on at such mine, quarry or other premises on or in connection with the said stone, without prejudice, however, to any rights or liabilities which may have previously accrued under this Scheme."

In order to obtain exemption under this paragraph the Secretary of State has directed (May, 1929) that the chemical analysis for the determination of silica (free and combined) in any sandstone shall be carried out in accordance with conditions specified by the Government Chemist, and the result shall be certified either by an analyst appointed by a local authority under the Food and Drugs (Adulteration) Act, 1928, or by an analyst approved by the Secretary of State.

The conditions specified by the Government Chemist were attached to the Home Secretary's notice; with some little modification they are as follows:

SANDSTONE INDUSTRY (SILICOSIS) SCHEME, 1929.*

DETERMINATION OF SILICA IN SANDSTONE AND ROCKS.

The method for the determination of total silica in sandstone and rocks at present in use is described in the following scheme. While the method applies in the majority of cases, some rocks may behave abnormally, and in these, special precautions are necessary. No general statement can be made applicable to all such cases.

SAMPLING.—A representative sample of the material should be taken by an expert sampler. The size of the sample will depend on the homogeneity and texture of the material.

PREPARATION OF SAMPLE FOR ANALYSIS.—The sample is broken into pieces of such a size that they may easily be inserted into the percussion mortar to be used in the later stages of pulverisation. After it has been thoroughly mixed, this broken material must be "quartered

* S.R. & O. 1929, No. 171. MASTER AND SERVANT. Workmen's Compensation Act, 1925, dated March 18, 1929. H.M. Stationery Office. Price 5d. net.

down" to a bulk of about half a pound, which is then crushed in a steel percussion mortar until the whole of it can pass through the topmost of a battery of six sieves whose mesh is graded from 5 I.M.M.† (topmost sieve) to 100 I.M.M.† (lowest sieve). The fractions retained by each sieve after a thorough shaking are separately mixed, weighed, and such aliquot portions taken from each that there is obtained a final combined sample of all grades, weighing not less than 10 grms. This is again shaken in the battery of sieves, and the coarser portions are crushed in the percussion mortar until the whole of it passes through the 100 sieve. The final powder is thoroughly mixed and transferred to a closed bottle. Gross particles of iron may be removed from this powder by means of a magnet.

DETERMINATION OF SILICA.—One gm. of the finely powdered sample is mixed with 4 grms. of pure anhydrous sodium carbonate in a platinum crucible, the mixture being covered with a further 1 gm. of the sodium carbonate. The crucible and contents are heated over a Teclu or Meker burner, at first gently, the heat being gradually increased to the full and so maintained for 20–30 minutes until the contents are in a state of quiescent fusion. After a final heating for 5 minutes over the blast, the crucible is cooled by quenching in cold water, and the fused cake is removed as far as possible and disintegrated by heating with water and one drop of alcohol in a platinum dish. Fifteen ml. of concentrated hydrochloric acid (sp. gr. 1.15) are then added slowly, the dish being covered, and after effervescence has ceased, the liquid is evaporated to dryness on a water or a steam bath, heating being continued until the bulk of the hydrochloric acid is removed and the deep yellow colour of the iron chloride has changed to a pale yellow. The dry mass is cooled and drenched uniformly with about 5 ml. of concentrated hydrochloric acid, 100 ml. of water added, and, after solution of the soluble salts by heating, the whole is filtered, and the silica washed, first with cold water and finally with hot, until free from chloride. The filtrate is again evaporated to dryness, the mass is treated with hydrochloric acid and water as in the first evaporation, and the small amount of silica is filtered off, and washed on a separate filter paper. The combined filter papers, and silica, etc., are dried, burned and finally ignited over the blast in a weighed platinum crucible until the weight is constant (A). A few drops of water, 5 drops of sulphuric acid (1:1), and 10 ml. of pure hydrofluoric acid are added to the crucible, and the silica volatilised by evaporation to dryness on a hot plate. The crucible and residue are ignited and weighed (B); the difference between (A) and (B) gives the weight of silica in the sandstone taken.

It is to be noted that the residue after volatilisation of silicon tetrafluoride may contain sulphates which are difficult to break up on heating. In such a case the residue must be ignited again after mixing with pure solid ammonium carbonate.

A blank experiment must be carried out at the same time, using the same number of filter papers and similar quantities of reagents.

† I.M.M. signifies the scale of sieves adopted by the Institute of Mining and Metallurgy.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Invertase from Honey. P. E. Papadakis. (*J. Biol. Chem.*, 1929, 83, 561–568.)—It has recently been shown by other investigators that invertase from honey differs from invertase from yeast in several ways. Honey invertase shows a characteristic difference from yeast invertase in the beginning of the hydrolysis of sucrose, being activated by β -glucose, whilst yeast invertase is not; and invertase preparations from honey do not hydrolyse raffinose, whereas invertase preparations from yeast do hydrolyse it. An investigation has now been made in order to obtain additional information concerning honey invertase and its properties. Since β -glucose activates honey invertase, the effect of other aldoses, such as

pentoses, on the rate of sucrose hydrolysis by honey invertase was studied. Experiments were also carried out on the retarding influence of mercuric chloride and α -methylglucoside on sucrose hydrolysis by honey invertase, and on the effect of β -glucose on sucrose hydrolysis by honey invertase in the presence of these retardants. The results seem to indicate that, in the case of honey invertase, sucrose hydrolysis is not activated by the pentoses, mutarotated xylose, *d*-arabinose and *l*-arabinose. Mercuric chloride does not retard the rate of sucrose hydrolysis much at P_H 5.7, but the retardation is more pronounced as the P_H decreases from 5.7 to 4.23. The influence of β -glucose is independent of the presence of mercuric chloride. In the presence of α -methylglucoside β -glucose accelerates the sucrose hydrolysis by honey invertase, and when the P_H is varied from 5.84 to 4.2 α -methyl glucoside does not cause much retardation, and does not change the characteristic sucrose hydrolysis curve. P. H. P.

Melecitose in Linden Dew Honey. F. E. Nottbohm and F. Lucius. (*Z. Unters. Lebensm.*, 1929, 57, 549–558.)—This substance, which has hitherto only been observed in manna and in dew honey (*cf.* Hudson and Sherwood, *ANALYST*, 1920, 45, 136), was separated from the sediment deposited in the latter by extraction of the water-soluble portion. The residue was dissolved in hot water, the dextrin precipitated with alcohol, and the filtered solution evaporated and allowed to crystallise. Melecitose is a trisaccharide, probably $3C_6H_{12}O_6-3H_2O$ (mol. wt. 481), with m.pt. 153 to 156° C., and it crystallises in non-hygroscopic masses of white plates or rhombic prisms. It has a slightly sweet taste, is sparingly soluble in water, alcohol and organic solvents, is oxidised by nitric acid to oxalic acid, and reduces Fehling's solution only to a very slight extent. It has a specific rotation of 89.5° (no muta-rotation), but on hydrolysis by 1 per cent. sulphuric acid for 1 hour at 70° C. this falls to 66.2°, on account of the formation of dextrose and turanose, $C_{12}H_{22}O_{11}$ (m.pt. 157° C.; osazone, m.pt. 216° C., with decomposition). On further hydrolysis turanose decomposes into dextrose and laevulose. Melecitose resists the action of fermentation enzymes or *B. coli*, and probably plays an important part in the metabolism of digestion. J. G.

Formol Titration in the Investigation of Honey. A. Gottfried. (*Z. Unters. Lebensm.*, 1929, 57, 558–560.)—The method of Tillmans and Kiesgen (*ANALYST*, 1927, 52, 417) has been tested on a large number of samples of honey, and the formol titration value (c.c. of 0.1 *N* sodium hydroxide solution for 20 grms. of honey in 100 c.c. of water) has been shown to vary from 0.3 to 1.1 for honeys which, according to the tests of Fiehe and of Ley, are suspect, and from 0.6 to 4.0 for genuine honeys. Lund's tannin precipitation figure increases with the formol titration value up to about the formol value 1.3, above which the correspondence is poor. J. G.

Some Organic Acids of Sugar Cane Molasses. E. K. Nelson. (*J. Amer. Chem. Soc.*, 1929, 51, 2808–2810.)—The acids of molasses have been determined and found to be formic acid, about 0.1 per cent., and acetic acid, 0.2 per cent.

(volatile acids); aconitic acid, 0.8 per cent.; lactic acid, 0.05 per cent.; and small quantities of malic and citric acids (non-volatile acids). The volatile acids were distilled from 3 kilos. of molasses to which sufficient hydrochloric acid had been added to liberate the combined acids. The distillate was neutralised with standard barium hydroxide solution and evaporated to dryness. The dried salts were weighed, and from this weight and the amount of barium necessary to neutralise the distillate, the proportion of barium formate and barium acetate was calculated. The ester distillation method was used for the determination of the non-volatile acids. They were first precipitated as lead salts from 2 kilos. of molasses. The acids recovered from the lead salts were dissolved in water and extracted 4 times with ether; the ether removed 4.06 grms. of crystalline aconitic acid (m.pt. 185–186° C.). The aqueous solution was then evaporated to dryness, esterified, and the esters (7.8 grms.) fractionated at 10 mm. Less than 1 c.c. distilled under 150° C.; this fraction afforded a hydrazide (m.pt. 178–179° C.), identified as malic hydrazide. Fraction 2 boiled at 160° C. This fraction was saponified, acidified, and extracted with ether, and yielded pure aconitic acid (3 grms.). The third fraction, boiling above 160° C., measured 0.5 c.c. With hydrazine hydrate it formed citric hydrazide (m.pt. 100–103° C.). A direct, continuous ether extraction was made on the acids recovered by precipitation of 3 kilos. of molasses with lead acetate, in order to avoid losses by esterification, and 23.9 grms. of aconitic acid were obtained. The acid solution remaining was neutralised with calcium carbonate, filtered, boiled, and the precipitate deposited was filtered off and dried. This calcium salt, (1.76 grms.) yielded citric acid (m.pt. 142–144° C.). Four hundred grms. of Dominican molasses were acidified, diluted with 200 c.c. of water, and extracted with a rapid stream of ether for 24 hours. The ether-soluble acids were neutralised with barium hydroxide, diluted to 100 c.c., and 200 c.c. of alcohol were added. After standing over-night the solution was filtered, treated with sulphuric acid to deposit barium sulphate, filtered, boiled with an excess of zinc carbonate, and filtered again. The filtrate was concentrated to 5 c.c., 15 c.c. of alcohol were added, and the crystalline precipitate was filtered off, dried, and weighed (0.315 gm.), and proved to be zinc lactate. All the fractions from fractional crystallisation of the acids recovered from the insoluble barium salt were found to be aconitic acid. The establishment of the presence of formic, acetic, aconitic, malic and lactic acids in sugar cane molasses confirms the results of previous investigators. The presence in sugar cane molasses of citric acid has not previously been reported.

P. H. P.

Tests for Methanol. H. Leffmann and C. C. Pines. (*Am. J. Pharm.*, 1929, 101, 584–586.)—Matthes' modification of the German process for the detection of methanol (*Pharm. Ztg.*, 1926, 96), whereby potassium guaiacosulphonic acid is substituted for guaiacol dissolved in strong sulphuric acid, is regarded very favourably. The U.S.P. (X) method is satisfactory, but glycerol (which is not infrequently present in factitious liquors) will simulate the methanol reaction, and, on distillation, glycerol, or some decomposition product thereof, will give a reaction with the magenta and sulphurous acid test; guaiacosulphonic acid, however, will not.

D. G. H.

Use of Ultra-violet Light in the Detection of Refined Oil in Virgin Olive Oil. S. Musher and C. E. Willoughby. (*Oil and Fat Ind.*, 1929, **6**, 15-16.)—

The fluorescence under the ultra-violet lamp (light reflected from the sample) of virgin olive oils varies from canary yellow to deep orange, that of second-pressing oils being darker, but all refined oils give a characteristic bluish-violet fluorescence. The ultra-violet lamp, used in conjunction with a spectro-photometer, can detect down to 5 per cent. of refined oil in virgin olive oil; without the aid of the spectro-photometer 65 per cent. of refined oil could not be detected. The differences of fluorescence are regarded as due to the varying amounts of chlorophyll present. Californian virgin oils more nearly resemble second-pressing oils from Europe, the reason suggested being the greater proportion of oil extracted from the fruit in the process, and the consequent difference in chlorophyll content. Heating a virgin oil for 30 minutes at 300° C. caused it to fluoresce like a mixture containing 5-10 per cent. of refined oil.

D. G. H.

Water in Strychnine Sulphate. W. Schnellbach. (*Amer. J. Pharm.*, 1929, **101**, 587-590.)—Crystallised strychnine sulphate may be either the pentahydrate (monoclinic crystals) formed when crystallisation occurs above 40° C., and containing theoretically 10.51 per cent. of water, or the hexahydrate (tetragonal crystals) when crystallised below 40° C., and having 12.36 per cent. water, and preparations with water contents deviating from the theoretical values of these two forms are considered to be mixtures of the two hydrates.

D. G. H.

Determination of Sparteine. J. Hirt. (*J. Pharm. Chim.*, 1929, **121**, 111-115.)—The gravimetric silicotungstic method of Bertrand (1899) is regarded as the most satisfactory for the determination of sparteine. Sparteine silicotungstate is somewhat soluble in water, and the optimum conditions for precipitation are in the presence of 1 per cent. acidity as sulphuric acid. The silicotungstic reagent itself has no influence on solubility.

D. G. H.

Colorimetric Determination of Strophanthins. A. Leulier and H. Griffon. (*Bull. Soc. Pharm.*, 1929, **36**, 408-414; *Ann. Chim. anal.*, 1929, **11**, 260-261.)—Liebermann's reaction is applied by treating a trace of the glucoside with 2 c.c. of acetic anhydride, followed by 2 c.c. of chloroform, and finally by 2 drops of concentrated sulphuric acid. The olive-green colour is at its maximum in 30 minutes, and the colour is given by all amorphous commercial strophanthins, but ouabain gives a yellow-orange colour. The reaction has also been studied quantitatively. As a modification of Pettenkofer's reaction, a trace of the glucoside is dissolved in 0.5 c.c. of absolute alcohol, 0.1 c.c. of 1 per cent. furfural solution in 95 per cent. alcohol is added, and 0.5 c.c. of concentrated sulphuric acid run in to the bottom of the tube. A blue ring is formed with amorphous glucosides at the point of separation, and a violet-grey ring with the crystallised glucosides.

D. G. H.

Biochemical.

Therapeutic Value of Irradiated Milk in the Treatment of Rickets.

C. Watson, T. Y. Finlay and J. B. King. (*Lancet*, Oct. 5, 1929, 704-707.)—

A series of observations has amply confirmed the claims of numerous German writers concerning the value of irradiated milk in the prevention and cure of rickets. For the work the Scholl and Scheidt methods of irradiation were tried, and milk was successfully irradiated by both these processes. The latter is known as "the cold process." Twelve cases of pronounced rickets were selected for treatment, four of which had been under skilled hospital treatment for periods ranging from 3 to 5 months, and had proved unusually refractory to treatment. All medicinal and other special antirachitic measures in use were stopped, the same diet being continued, with the exception that 6 oz. daily of irradiated milk replaced 6 oz. of the 18 oz. of non-irradiated high-grade milk in previous use. The other 8 cases were each given 18 oz. of irradiated milk daily and 18 oz. of non-irradiated milk. Frequent radiological examinations were made at short intervals; attention was directed mainly to the condition of the wrists, knees and ankles. Rapid improvement took place; within 14 days of starting to give irradiated milk it was clear that a remarkable curative influence was at work. In cases of moderate severity radiological evidence of cure was obtained within 4 to 6 weeks, and in extreme cases within 6 to 8 weeks. A strange feature of one very severe case was the coincident improvement which occurred in the mental development of the child; this did not develop noticeably until after 3 weeks' treatment. The authors believe that there could be no justification for the price of irradiated milk exceeding that of non-irradiated milk by more than 1d. per pint. Irradiated milk should be used with care and discrimination. In this country irradiated milk can only be sold under license from the patent holders. Under this arrangement the licensees agree that "their irradiated milk shall not contain less than two (2) ostelin (vitamin D) units per gramme of butter-fat as determined by the P_H drop test under conditions laid down in the papers by Jephcott and Bacharach (*Biochem. J.*, 1926, xx, 1351; 1928, xxii, 60), or, alternatively, eight (8) Pharmaceutical Society's units per gramme of butter-fat as adopted in test by the Pharmaceutical Society." With fuller knowledge, time may show that these tests may require modification. We have at present no assurance that the butter-fat supplies a complete and reliable guide. However, under the existing standards, milk definitely can be successfully irradiated so as to have imparted to it a very valuable additional therapeutic property in the prophylaxis and cure of rickets. Irradiated milk should not be regarded as a complete substitute for good fresh untreated milk. In rickets, between 2 and 5 years of age, excellent results have followed its use when the milk has been used in strengths varying from 1 part irradiated to 2 parts non-irradiated, up to equal parts of the two preparations. The cure of the disease is established more quickly, effectively, and economically by the use of irradiated milk than by various irradiated commercial preparations. There are indications that irradiated milk may prove of outstanding

value in the treatment of certain disorders other than rickets, notably disorders incidental to pregnancy and lactation, the climacteric, malnutrition, injuries and surgical diseases of bone, and certain forms of tuberculosis. The authors consider that there is need for the establishment in this country of a scientific body to initiate and direct the work, both on its strictly scientific and clinical sides, called for by these new facts about nutrition and the influence of ultra-violet rays upon it.

P. H. P.

Heat and Ultra-Violet Irradiation as Means of Differentiating Vitamins B and G in Yeast. C. Kennedy and L. S. Palmer. (*J. Biol. Chem.*, 1929, 83, 493-496.)—Vitamin *B*, the antineuritic factor, and vitamin *G*, the antipellagric factor, are both necessary for growth; an accurate practical method for the isolation of each factor is, therefore, highly desirable. Hogan and Hunter (*J. Biol. Chem.*, 1928, 78, 433; *ANALYST*, 1928, 53, 505) proposed what seemed to be a promising method for destroying the antipellagric vitamin and leaving intact the antineuritic vitamin in yeast. They found that yeast, irradiated under certain conditions, loses its so-called growth-promoting properties, and retains its antineuritic activity, and that autoclaved yeast, which possesses no antineuritic potency, corrects the deficiency of the irradiated yeast. The authors, in continuing their investigations on yeast (*J. Biol. Chem.*, 1928, 76, 591) as a source of the growth-promoting factors, have not been able to substantiate these results of Hogan and Hunter. Irradiated yeast, as a source of the growth-promoting factors, vitamins *B* and *G*, has been tested both alone and in conjunction with autoclaved yeast. A figure gives the composite growth curves obtained with the feeding trials. The control group of rats, Lot 1, received daily 0.5 gm. of untreated dry starch-free yeast to supply vitamins *B* and *G*, those of Lot 2 autoclaved yeast, those of Lot 3 irradiated yeast, and those of Lot 4, 0.5 gm. of a mixture of equal parts by weight of autoclaved and irradiated yeast. The rate of growth of the rats in Lot 3, as shown by the graphs, was very good; thus irradiation could not have completely destroyed the antipellagric factor. The rate of growth of the rats in Lot 4 did not quite equal that of the rats in Lot 1. It is very probable, therefore, that irradiation and autoclaving impair in varying degrees both vitamin *B* and vitamin *G*. Two further groups of rats were given a ration that differed from the others in that it contained, in addition, the alcoholic extract of 15 grms. of ether-extracted wheat embryo; this ration was thought to contain ample quantities of vitamins *B* and *G*, but it failed to promote growth, and became growth-promoting when small quantities of autoclaved yeast were added. The curves of Lot 5 show that this ration also became growth-promoting when supplemented with the irradiated yeast; an additional supplement of autoclaved yeast (Lot 6) did not enhance the rate of growth over that of the irradiated yeast alone. Therefore, irradiation cannot be relied upon completely to destroy the growth-promoting factors of yeast other than the antineuritic factor.

P. H. P.

Quantitative Studies of Responses to Different Intakes of Vitamin D. H. C. Sherman and H. K. Stiebeling. (*J. Biol. Chem.*, 1929, 83, 497-504.)—A quantitative study has been made of the effect of graded allowances of vitamin *D*

upon growth and calcification in young rats receiving a basal diet adequate in other respects, but decidedly deficient in vitamin *D*. The diet used consisted of extracted casein, 18 per cent.; Osborne and Mendel salt mixture, 4 per cent.; dry brewers' yeast, 10 per cent.; sodium chloride, 1 per cent.; dried spinach, 1 per cent.; and corn-starch, 66 per cent. The results show that in young rats reared by mothers on a diet consisting largely of two-thirds ground whole wheat, and one-third whole milk powder, and transferred at the 21st or 28th day of age to the vitamin-*D*-deficient diet, practically normal calcification resulted by the 56th day of age in cases in which the basal diet had been supplemented by somewhat more than 5 per cent. of the calories from whole (summer) milk powder, and by the 80th day of age in cases in which the basal diet had been supplemented during the preceding 4 weeks by the same milk powder to the extent of 8 to 9 per cent. of the calories. Smaller graded portions of milk produced corresponding improvements in calcification over their respective negative controls. The experiments reported afford extensive and convincing evidence in confirmation of the fact that cow's milk as ordinarily produced in the U.S.A. contains important amounts of vitamin *D*. The deposition of calcium in the femurs appears to be more closely proportional to the supplementary vitamin *D* furnished than does gain in weight. The improvement in growth, due to additional vitamin-*D*-containing material between the 21st and 56th days, is too small for the growth during that period to be used as a quantitative measure of the vitamin *D* furnished; however, a figure shows that after giving the vitamin *D*-deficient diet for a month, grading the allowance of vitamin *D* is then reflected by the gain in weight. There is additional evidence that the test animals had considerable bodily stores of vitamin *D* which must have come from the milk consumed by themselves and their mothers. Equally consistent responses in calcification were obtained under the conditions of these experiments when the experimental period followed immediately upon separation of the young from their mothers as when it was preceded by prolonged feeding of the vitamin *D*-deficient diet. This procedure insures vigorous animals, and permits the 4- or 5-week experimental period to be terminated at an early age, thus making use of the period of most rapid deposition of calcium, as well as reducing the time and expense involved in experimental work. The percentage of calcium in the fresh femur is proportional to the supplementary vitamin *D* furnished within a sufficient range of values to permit of reasonably quantitative comparisons, when sufficient numbers of well-controlled experiments are performed. P. H. P.

Toxicological.

New Derivatives of *p*-Phenylenediamine and their Value as Hair-Dyes. H. Meyer. (*Chem. Ztg.*, 1929, 53, 765-766.)—Para-phenylenediamine, formerly used for dyeing hair, has an irritant action on the skin, whereas the less markedly basic *p*-toluylenediamine, *p*-aminodiphenylamine and phenylenediamino-sulphonic acids cause little, if any, such action. Moreover, since those whose heads perspire intensely are particularly prone to hair-dye dermatitis, this trouble

is probably due to the formation of salts of the diamine with the perspiration acids. Under conditions similar to those prevailing on the head, *p*-phenylenediamine, *p*-toluylenediamine, and *p*-aminodiphenylamine all form salts with butyric acid, but this salt-formation proceeds readily and considerably only with the first of these bases. Various compounds of these bases with carboxylic acids, such as salicylic, gallic and benzoic, when mixed with hydrogen peroxide solution, exhibit satisfactory hair-dyeing properties, and result in no harmful effects.

T. H. P.

Methyl Chloride Poisoning. **Kegel, McNally and Pope.** (*J. Amer. Med. Assoc.*, Aug. 3, 1929, 353; *Brit. Med. J.*, Oct. 5, 1929, 633.)—Methyl chloride is used to a very large extent in domestic refrigerators in America, and has been found to be the cause of much illness and many deaths. It is odourless, and, therefore, all the more dangerous. It is decomposed in the human body into methyl alcohol, which destroys nervous tissue and causes degenerative changes in the heart, liver and kidneys. The symptoms are drowsiness, and nausea with vomiting. Blood appears anæmic, and the urine may contain formic acid, diacetic acid and acetone. Halogen derivatives of aliphatic hydrocarbons appear to be more toxic than the hydrocarbons themselves, not by the action of the halogen alone, but of the whole molecule.

R. F. I.

Agricultural.

Determination of Ammonia in Soil and the Adsorption Power of Soil for Ammonia. **C. Olsen.** (*Compt. rend. Lab. Carlsberg*, 1929, 17, No. 15, 1–20.)—The determination of ammonia in soils by direct distillation with alkali is suspect on account of the liberation of the ammonia from nitrogen in the organic matter present, while extraction by water is incomplete under ordinary conditions, owing to adsorption of ammonia by the soil. It is, therefore, proposed that 100 grms. of fresh broken soil (or 50 grms. of peat) should be shaken in a bottle for 1 hour with a few drops of toluene, 200 c.c. of *N* potassium chloride solution and sufficient hydrochloric acid (determined by trial with Congo red paper) to bring the P_H of the suspension to 1.0 ± 0.3 . The P_H of the filtered extract is determined by means of methyl violet, and the correction $+0.45$ applied for the salt error of potassium chloride. Ammonia is determined by distillation of 100 c.c. with 200 c.c. of water and 4 grms. of magnesia into an excess of standard sulphuric acid, which is then boiled and back-titrated. Allowance must also be made for the blank on the reagents and for the water-content of the soil. If the contents of the distillation flask are then again diluted to 300 c.c. and 3 grms. of Devarda alloy added, the nitrate nitrogen may be determined on the same portion of the filtrate. Comparative extractions with water and with the above salt solution of 2 peat, 2 clay and 2 sandy soils (P_H values 3.7 to 7.6) showed that the adsorption capacities for ammonia decreased in the order mentioned, irrespectively of the P_H value, and that most ammonia is adsorbed when the total ammonia content of the soil is highest.

J. G.

Organic Analysis.

Chia Seed Oil. W. F. Baughman and G. S. Jamieson. (*Oil and Fat Ind.*, 1926, 6, 15–17.)—Oil from the seed of the Mexican chia plant (*Salvia hispanica*, L.) had the following characteristics:—Sp. gr. $25^{\circ}/25^{\circ}$, 0.9358; n_D^{20} , 1.4838; saponification value, 194.8; iodine value (Hanus), 190.0; thiocyanogen-iodine value, 113.2; unsaponifiable matter, 0.7 per cent.; acid value, 1.4; loss of weight on heating 3 hours at 110° in carbon dioxide, 0.3 per cent.; hexabromide number of fatty acids, 51.2; saturated acids (corrected), 8.1; unsaturated acids (corrected), 85.2 per cent., of iodine value 214.6. The composition of the unsaturated acids in the original oil was: linolenic, 39.3; linolic, 45.2; and oleic acid, 0.7; and of the saturated acids: myristic, 0.14; palmitic, 4.90; stearic, 2.73; and arachidic, 0.33 per cent.

D. G. H.

Malayan Lumbang Oil. T. H. Barry. (*J. Soc. Chem. Ind.*, 1929, 48, 239T–290T.)—A sample of lumbang oil from nuts grown on the Government experimental station at Serdang in the Malay States had the following characteristics:—Sp. gr., 0.9264; n_D^{20} , 1.4764; saponification value, 192.1; iodine value, 150.8; unsaponifiable matter, 0.41 per cent.; acid value, 0.66; and coefficient of expansion at 12.5 – 46° C., 0.00063. The iodine value is lower than that recorded for Phillipine oil. It was possible to detect with certainty lumbang oil added to China wood oil by using the Brown heat test; but the maximum limit of 12 minutes is not exceeded until 20 per cent. is present. Lumbang oil alone is not suitable as a paint medium in this country, although it might be in a drier and warmer climate. The drying time under laboratory conditions was double that of linseed oil. D. G. H.

Separation of Cystine from Histidine. H. B. Vickery and C. S. Leavenworth. (*J. Biol. Chem.*, 1929, 83, 523–534.)—In acid solution cystine forms a silver compound which becomes increasingly insoluble as the acidity of the solution is reduced. At P_H 6.0 nearly all the cystine present in such a solution is precipitated. Data are given which show that this amino acid is precipitated more or less completely by every heavy metal reagent that is customarily used to throw down histidine; it is, therefore, probable that cystine has been present as an impurity in the final histidine fractions secured in most protein analyses. The copper compound of cystine is very insoluble, and separates readily and completely when a solution of cystine is boiled with an excess of copper hydroxide and cooled. Under the same circumstances histidine remains in solution. Therefore to separate these two amino acids the solution containing them is boiled for 30 minutes with excess of copper hydroxide, allowed to stand at least 30 minutes, and then filtered to remove the cystine copper and excess copper hydroxide. Copper is subsequently removed from the filtrate by hydrogen sulphide, and the solution is treated in the usual way for the determination of histidine as dinitronaphtholsulphonate. Histidine fractions can be determined with greater ease and accuracy by this procedure. The precipitation of cystine by copper hydroxide was investigated both with preparations of pure plate cystine ($[\alpha]_D^{20} = -215^{\circ}$) and partially racemised

“needle cystine” ($[\alpha]_D^{20} = -41^\circ$), and both compounds were almost completely precipitated. Colorimetric determinations for cystine were carried out on the filtrates after removal of the copper. As an illustration of the application of this procedure, an analysis of the basic amino acids of human hair has been carried out, which indicates that this tissue yields 0.5 per cent. of histidine, 8.0 per cent. of arginine, and 2.5 per cent. of lysine. A colorimetric determination of cystine on the same sample indicated that 16.5 per cent. of cystine was present. P. H. P.

Inorganic Analysis.

Use of Phenolic Acids in the Detection, Separation and Determination of Metals. Part I. Separation of Group 2A Metals. P. N. Das-Gupta. (*J. Indian Chem. Soc.*, 1929, 6, 627–633.)—(a) The precipitated sulphides of mercury, bismuth, lead, copper and cadmium are digested with 6 N nitric acid, the residue tested for mercury, and the filtrate boiled to remove hydrogen sulphide, neutralised with sodium hydroxide till a permanent turbidity appears, again boiled, and a slight excess of a fresh 1 per cent. gallic acid solution added. Bismuth may then be filtered off as a light yellow crystalline precipitate, and the filtrate (diluted if much bismuth or cadmium is present) boiled with a slight excess of sodium acetate solution to precipitate lead and copper, whilst the cadmium remaining in solution is precipitated as sulphide. Lead and copper are separated by the action of hydrogen peroxide and an excess of ammonia, which dissolve the latter in hot solutions. (b) If the metals are in nitric acid solution, sodium hydroxide is used to render the reaction faintly acid, an excess of a fresh solution of β -resorcylic acid added, and the mixture boiled and well stirred. Mercury gives a white or yellow precipitate, soluble in acid, and the filtrate may be treated as before. The optimum conditions for the reaction of these phenolic acids, with the metals concerned, have been examined in detail. J. G.

Volumetric Method for Determining Silver in Presence of Halides and Cyanides. H. Baines. (*J. Chem. Soc.*, 1929, 2037–2041.)—None of the known methods is applicable directly to the routine determination of silver occurring as halides in photographic products containing cyanides and small unknown and variable amounts of other substances which react with cyanide. If the silver is dissolved in a slight unknown excess of potassium cyanide solution and standard iodine is run in until one drop produces a faint permanent opalescence, the excess of potassium cyanide has then completely reacted with the iodine, $KCN + I_2 = KI + CNI$. If now starch is added and the titration with iodine continued until a permanent blue colour appears, the silver complex has reacted completely with the iodine, $KAg(CN)_2 + 2I_2 = KI + AgI + 2CNI$. Thus, the volume of iodine added between the two stages determines the silver, and the total iodine added the cyanide. The opalescence is better defined if an electrolyte is present.

A quantity of material containing 0.05 to 0.09 grm. of silver is dissolved in 5 to 9 c.c. of approximately 0.2 N potassium cyanide solution containing 5 c.c. of

ammonia (0.880) per litre, 50 c.c. of 10 per cent. sodium chloride solution being added, and 0.1 *N* iodine solution run in from a burette until a faint opalescence persists; if this point is over-run, it may be re-adjusted after addition of a little cyanide solution—in known quantity if cyanide is to be determined. The liquid is now diluted to 900–1000 c.c. (or correspondingly more if more cyanide than the quantity given were added) with tap water, and 5 c.c. of 0.5 per cent. starch solution are added, the titration being continued till a permanent blue colour appears. The method gives consistent and accurate results. T. H. P.

Separation of Lead and Bismuth. H. Blumenthal. (*Z. anal. Chem.*, 1929, 78, 206–213.)—The sample (10 grms.) is dissolved in dilute nitric acid (16 c.c. of acid, sp. gr. 1.4 and 60 c.c. of water), cooled, diluted to 150 c.c. and a 10 per cent. solution of sodium carbonate added, till all the lead carbonate is precipitated. It is then re-dissolved by addition of sufficient acid to render the solution acid to methyl orange, and the carbon dioxide boiled out. A paste of mercuric oxide is then freshly prepared from pure sodium hydroxide and 5 per cent. mercuric chloride solutions, washed free from alkali by decantation with water, and a slight excess added to the solution with 100 c.c. of cold water. After 12 hours the precipitate, which contains basic bismuth nitrate, is filtered off, the filtrate re-treated with mercuric oxide if it is still turbid, and the precipitate washed with 0.1 per cent. potassium nitrate solution till the washings give no lead sulphate precipitate with sulphuric acid. It is then dissolved in nitric acid, and the bismuth determined colorimetrically by the iodide method. If bismuth is present in relatively large quantities, the final acid solution (100 c.c.) is boiled, and 20 c.c. of a 5 per cent. solution of ammonium phosphate added, a drop at a time, and the bismuth phosphate filtered from the cool solution and weighed. The bismuth was recovered completely from mixtures of 8 grms. of lead nitrate with 0.3 to 50 mgrms. of bismuth, and from mixtures containing 50 per cent. of each metal. Slight modifications are necessary in the presence of arsenic, antimony and tin, and methods of removal of these metals are described. J. G.

Application of the Thiocyanate Method for the Precipitation of Copper in the Confirmatory Tests for Cadmium and Antimony. A. F. Daggett. (*J. Amer. Chem. Soc.*, 1929, 51, 2758–2759.)—The insolubility of cuprous thiocyanate in dilute sulphuric and hydrochloric acids and the ease of precipitation make the thiocyanate method well suited for application to the qualitative scheme of analysis. The means for the separation of copper from cadmium in the confirmatory test for cadmium given by Noyes, "*Qualitative Chemical Analysis*" (1928, 80), has not been found satisfactory for demonstration purposes, but the following thiocyanate method has given very satisfactory results: To the part of the ammonium hydroxide solution, which remains after the ferrocyanide test has been made for the confirmation of copper, dilute sulphuric acid is added until the solution is acid to litmus, and then 5 c.c. of *N* potassium thiocyanate solution; a brown coloration results, due to the formation of cupric thiocyanate. The solution is heated to boiling, about 0.5 gm. of dry sodium sulphite is added, and boiling

continued for about 1 minute, until the white precipitate of cuprous thiocyanate has coagulated. The precipitate is then filtered off, and the clear filtrate is saturated with hydrogen sulphide, when the characteristic yellow precipitate of cadmium sulphide forms if cadmium is present. To avoid the interference of copper in the test for antimony, as given by Noyes, this procedure may be used to advantage after the antimony and tin have been separated from the arsenic by concentrated hydrochloric acid, and the solution has been diluted to the proper acid concentration for the precipitation of the antimony sulphide. P. H. P.

Volumetric Determination of Tin. H. Wolf and R. Heilingötter. (*Chem. Ztg.*, 1929, **53**, 683.)—For tin-antimony alloys 0.1 to 0.4 gm. is warmed with a mixture of 50 c.c. of hydrochloric acid (sp. gr. 1.19) and 10 c.c. of a solution of ferric chloride (100 grms. in 50 c.c. of HCl of sp. gr. 1.12), and the tin then completely reduced to the stannous state by the action of 3 iron nails, 8 cm. long, in the presence of 50 c.c. of water and in an atmosphere of carbon dioxide on the water bath for 8 minutes (for 0.1 gm. of tin). The cool solution is filtered on a folded paper sprinkled with *ferrum redactum*, the paper washed, and the filtrate titrated with 0.1 N iodine solution with a starch indicator. For copper-tin alloys 1 to 3 grms. of metal are dissolved in 10 c.c. of concentrated nitric acid, the diluted solution filtered, and the residue washed with hot water, dried, mixed with sodium peroxide, and strongly ignited in an iron crucible. The residue is extracted with water, and sufficient hydrochloric acid (sp. gr. 1.19) added to dissolve the iron hydroxide and produce a 50 per cent. acid solution, and reduction carried out as above. Lead-tin alloys (3 to 5 grms.) are digested with 50 c.c. of hydrochloric acid, and the residue treated with potassium chlorate in the presence of a little more acid. The total soluble portion is made up to 500 c.c. in 50 per cent. acid, filtered, and reduced as before.

J. G.

Study of the Use of Aurintricarboxylic Acid for the Colorimetric Determination of Aluminium. O. B. Winter, W. E. Thrun and O. D. Bird. (*J. Amer. Chem. Soc.*, 1929, **51**, 2721–2731.)—The spectrographic method for the determination of small amounts of aluminium has an advantage over colorimetric methods in that it requires no chemical reagents, for aluminium contaminates nearly all reagents; but the apparatus is very expensive. Of the colorimetric methods which have been proposed, the most promising is the one making use of the ammonium salt of aurintricarboxylic acid, the dye commercially known as aluminon. Attempts to determine the aluminium in plants by modifications of this method used by various investigators did not give satisfactory results. A further study was, therefore, made of the reaction between aluminium and the dye, and the method has now been modified so that samples ranging from 0.0050 to 0.0700 mgm. of aluminium may be compared with one standard, and the amount of aluminium in each sample may be read directly from a curve. The results are accurate to within about 5 per cent. Special emphasis was placed on the determination of suitable conditions (1) for the formation of a lake of maximum colour intensity, and (2) for destroying the colour of the excess dye while retaining the

lake colour. Maximum colour intensity was obtained in the presence of 10 per cent. of 6 *N* ammonium acetate when the solution was at approximately P_H 4.0, and kept at a minimum temperature of 80° C. for about 10 minutes. In the presence of 5 c.c. each of 5 *N* ammonium acetate and ammonium chloride the dye changed colour at about P_H 7.0. A neutral or alkaline solution of 2 c.c. of 0.1 per cent. dye in a volume of 50 c.c. was very nearly colourless. The lake colour remained sufficiently permanent for determinations to be made until the solution was raised to P_H 7.4. The presence of ammonium acetate and chloride as buffers was found advantageous for controlling the P_H of the solution. Ammonium carbonate was found to be more suitable for the decolorisation of the excess dye than either ammonium hydroxide or a solution of ammonium carbonate in ammonium hydroxide. The procedure for aluminium determinations is as follows:—The solutions, which should be slightly acid, are transferred to 50 c.c. volumetric flasks, and each made up with water to about 20 c.c.; then 5 c.c. of 5 *N* ammonium acetate, 5 c.c. of 1.5 *N* hydrochloric acid and 2 c.c. of 0.1 per cent. dye are added, and the flasks are placed in a water-bath at about 80° C. for 10 minutes. Five c.c. of 5 *N* ammonium chloride are then added, the flasks cooled to room temperature, 5 c.c. of 3.2 *N* ammonium carbonate added, with gentle shaking, distilled water added to the mark, and the contents of each flask mixed. The reactions should then be P_H 7.1–7.3, and the red colour of a blank should disappear in about 15 minutes. (The exact concentration of the reagents is not important, but the final P_H is, and the amount of ammonium carbonate necessary to give this P_H should be found by neutralising similar solutions without adding the dye). A standard (or standards) containing a given quantity of aluminium should be treated simultaneously. After standing for 20 minutes for the excess dye to become decolorised, the colour intensities are compared, and the amounts of aluminium are read from a curve plotted as follows:—When a small number of determinations are to be made, four standards containing 0.0100, 0.0300, 0.0500 and 0.0700 mgrm. of aluminium, respectively, are prepared, and these are treated like the samples. All these solutions are compared with the standard containing 0.0300 mgrm. of aluminium, and the results are calculated to a colorimeter reading of 30 for this standard. Arbitrarily 0.0050 mgrm. of aluminium is given a reading of 100, and with this and the 4 readings of the standards a curve is plotted (colorimeter readings against mgrms. of aluminium), from which the quantities of aluminium in the samples are read. For a large number of determinations, over a period of time, several series of standards should be determined, and a curve plotted from the averages; then only one standard need be used each time determinations are made, and results may be read from the same.

P. H. P.

Electro-Analytic Determination of Thallium as Thallic Oxide. A. Jílek and J. Lukas. (*Collect. Trav. Chim. Czechoslovak*, 1929, 1, 417–428.)—The solution containing less than 0.25 grm. of thallium as thallic nitrate is electrolysed in a platinum dish (anode) in the presence of 1 to 2 grms. of 40 per cent. hydrofluoric acid, with a rotating platinum disc as cathode, at 2 to 5 volts and a

current density of 0.2 amp./cm². After 1 hour the thallium is completely deposited, but on both electrodes, and is removed from the cathode by addition of 1 c.c. of 30 per cent. hydrogen peroxide, without interrupting the electrolysis. It is then re-deposited on the anode as the compound Tl₂O₃.HF, which was found by analysis to contain 84.44 per cent. of thallium. Additions of hydrogen peroxide are necessary at the end of every hour till the electrolyte gives no reaction for thallos ions with potassium iodide or sodium sulphide (usually after 4 hours). The deposit is washed with water without interruption of the current, rinsed with alcohol and dried at 110° C. The fall in voltage produced, on addition of the peroxide, is recovered when this has decomposed. High results are obtained in the presence of alkali salts, especially sulphates, which are retained in the anodic deposit, although traces of thallium remain in solution. In such cases thallium should be removed as thallos sulphide, by the action of sodium sulphide on a hot solution of thallos nitrate and sodium carbonate, and re-dissolved in nitric acid.

J. G.

Determination of Strontium and Barium. L. Szebellédy. (*Z. anal. Chem.*, 1929, 78, 198-206.)—A solution containing 0.5 gm. of the mixed nitrates is evaporated with 50 c.c. of sulphate-free hydrobromic acid, the residue dried for 1 hour at 100° C. and extracted with 3 c.c. and 7 c.c. portions of *iso*-butyl alcohol, the mixed bromides being heated with the alcohol in a dish placed in a closed block of lead maintained at 110° C. for 10 minutes (*cf. id.*, 1927, 70, 39). The mixture is then transferred to a suitable filter moistened with the alcohol, and the clear filtrate evaporated in a tared dish, dried at 100 to 110° C., and dissolved in a minimum amount of water, which is then saturated with an excess of ammonium sulphate. The residue, after evaporation, is dried at 100° C. for 30 minutes, and heated, gently at first, and then strongly, for 20 minutes after fuming has ceased, and the cool residue weighed as strontium sulphate. The barium bromide is removed from the filter in 25 c.c. of hot water, the solution concentrated on the water-bath, and sufficient hydrobromic acid added to make a total of 1 gm. It is then washed into a tared covered dish, evaporated, dried at 180° C. for 30 minutes, and re-dried after addition of a drop of butyl alcohol, cooled and weighed.

J. G.

Analysis of Japanese Allanite. Y. Minami. (*Japanese J. Chem.*, 1929, 4, 1-5.)—The sample was powdered in an agate mortar, 1 gm. decomposed by concentrated hydrochloric acid, and the silica rendered insoluble by repeated evaporations and filtered off. Rare earths were removed from a hydrochloric acid solution of the precipitate produced with ammonia in the presence of ammonium chloride by precipitation with oxalic acid, and iron was then precipitated as sulphide in the filtrate in the presence of tartaric acid. After decomposition of organic matter in the new filtrate by means of hot sulphuric and nitric acids, aluminium and titanium were obtained as hydroxides and weighed as oxides, the titanium being determined colorimetrically after fusion of the oxide mixture with potassium bisulphate. The precipitate of rare earth oxalates was ignited, and the resulting oxides converted into nitrates, thorium being separated by addition of hydrogen

peroxide, whilst cerium was precipitated as iodate. The new filtrate was then saturated with potassium sulphate and the yttrium and cerium groups separated. Other metals were determined in the usual way, and the formula $4R''O$, $3R'''O_3$, $6SiO_2$, H_2O was derived from the analysis, where R'' is Ca, Mn or Fe, and R''' is Al, Fe, Ce, Y, etc. Analysis of the arc and absorption spectra of each fraction revealed germanium (in the tin fraction), holmium, erbium, thulium, praseodymium, neodymium, dysprosium, lanthanum, samarium, and ytterbium. J. G.

Micro-determination of Selenium and Tellurium in Organic Compounds. H. D. K. Drew and C. R. Porter. (*J. Chem. Soc.*, 1929, 2091–2095.)—

In the determination of selenium in organic compounds by converting it into the dioxide by heating with nitric acid in a Carius tube and subsequently precipitating the selenium by means of sodium sulphite, it is found to be unnecessary to remove the nitric acid. Passage of sulphur dioxide into the solution in presence of excess of hydrochloric acid suffices to destroy the nitric acid and to bring about, after an interval, the quantitative precipitation of selenium.

From 5 to 20 mgrms. of the material (3 to 5 mgrms. of selenium) are decomposed in a micro-Carius tube with about 0.3 c.c. of fuming nitric acid (d 1.5). The contents of the tube are washed into a boiling tube with alternate rinsings of water and concentrated hydrochloric acid, and the liquid (about 10 c.c.) is heated on a boiling water-bath while a stream of sulphur dioxide is passed through it. When the whole of the selenium is transformed into the black variety (about 20 mins.), the liquid is cooled and filtered through a Pregl micro-Gooch crucible (provided with a capillary cap to stabilise the humidity condition of the asbestos) with the aid of a siphon tube, the vessel and delivery tube being thoroughly rinsed with water and alcohol. The capped tube is dried at 110° during ten minutes in a stream of filtered air, and weighed with the usual precautions. The contents of the filter need not be changed for a further estimation, even after long standing; but, after 24 hours, the filter should be re-washed with water and alcohol, dried and again weighed before use. Not less than about 2.5 mgrms. of selenium should be weighed.

With a tellurium compound, 10 to 15 mgrms. are decomposed with fuming nitric acid (d 1.5) in a Carius tube (0.3 c.c. of acid) or a micro-Kjeldahl flask (3–4 c.c. of acid), the liquid being then rinsed into a small porcelain dish with water, and evaporated to dryness on a water-bath. The residue is dissolved in 3 c.c. of 10 per cent. hydrochloric acid and the solution evaporated to a syrup. The dish is covered with a small clock-glass, and 10 per cent. hydrochloric acid (3 c.c.) is added, followed by freshly prepared, saturated aqueous sulphurous acid (3 c.c.) and 15 per cent. aqueous hydrazine hydrochloride (2 c.c.). The mixture is heated for ten minutes on a water-bath with gradual addition of more sulphurous acid (2 c.c.), and the tellurium is then filtered off and washed with hot water and alcohol. The crucible is dried and weighed as with selenium. Precipitated selenium and tellurium show no tendency to oxidise.

Chlorine, bromine and iodine may be determined accurately on a micro-scale, even in presence of tellurium. Chlorides and bromides may be decomposed by heating in micro-Kjeldahl flasks with concentrated nitric acid containing excess of silver nitrate, but iodides should be decomposed with aqueous halogen-free potash before the iodine is precipitated, in the cold, with nitric acid containing silver nitrate. Fuming nitric acid should not be used, as it causes minute but appreciable losses of halogen, whether tellurium is present or not. T. H. P.

Physical Methods, Apparatus, etc.

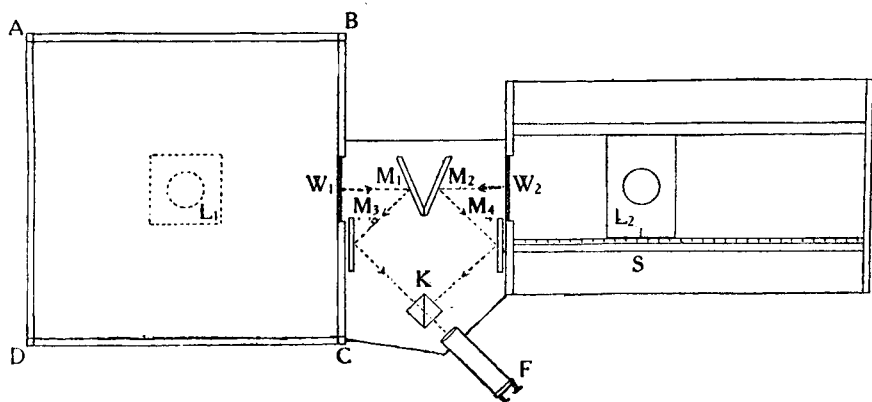
Distinction of Pigments in Ultra-Violet Light. M. J. Schoen and J. Rinse. (*Chem. Weekblad*, 1929, 26, 321-322.)—The examination of a large number of white pigments has shown that great care must be exercised in drawing conclusions from the results, as different samples of the same pigment (*e.g.* lithopone) may show different colours if they are of different origin. Also, so-called pure zinc whites containing less than 2 per cent. of lead white had the same fluorescence as zinc white of high lead white content. The fluorescence of zinc white may vary between green, brown and light yellow, whilst that of lead white is green-brown, though of less intensity. Natural chalk was distinguishable from precipitated chalk in the authors' samples, as the former appeared dark yellow and the latter black. Aluminium hydroxide showed a fine light-blue colour, and titanium-zinc oxide pigments (with one exception) bright violet, whilst organic dyes (*e.g.* imitation red lead) were easily recognisable. There is no relation between the fluorescence of lithopone and its fastness to light. J. G.

Cube Photometer for Comparing the Whiteness of Fabrics. A. Adderley. (*J. Text. Inst.*, 1929, 20, T203.)—The photometer described measures not only the total amount of light reflected by a fabric (intensity), but also the distribution of the light reflected by the surface of a fabric at various angles (colour). The latter specifies the lustre or "finish" of the surface. The apparatus consists of a hollow cube ABCD, 14" internal measurement, the interior of which is painted with several coats of a special zinc oxide paint having a reflection factor of 94 per cent., which is greater than that of any fabric yet found. The faces AB, CD, DA are detachable, and may be covered with the material under examination. The face BC is fitted with an opal window W_1 , 2 sq. in. The top of the cube has a central circular hole through which shines a 12-volt gas-filled lamp L_1 , casting a circle of illumination on the floor of the cube, no other part of the interior being directly illuminated. The photometric arrangements consist of a Lummer-Brodhun prism, K, and the mirrors M_1 to M_4 . A second opal window is fitted at W_2 , and is illuminated by the lamp L_2 , similar to, and in series with, L_1 , on a 24-volt accumulator, and moving over a scale S, which indicates the distance from the lamp to W_2 . Lamp L_2 is moved until W_1 is of the same illumination as W_2 , and the reading on scale S is noted. The brightness of W_2 is proportional to $1/d_1^2$

where d is the scale reading, and whence the brightness of W_1 can be calculated.

If one of the painted faces is now covered with fabric and the lamp again adjusted till the windows are equally illuminated, a new brightness figure is obtained $1/d_2^2$. The reflection or intensity factor compared with that of the paint can be written as a function of $\left(\frac{d_1}{d_2}\right)^2$.

The measure of the intensity is expressed as a percentage of the light which would be reflected from the specially painted surfaces. This measure, however,



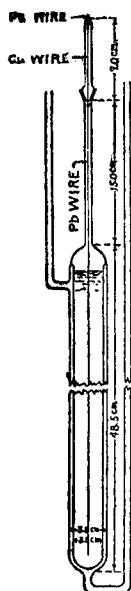
does not describe the manner in which the fabric departs from white. It is conceivable that two fabrics, one on the yellow side and one on the blue side, would give the same intensity.

The *colour* can be measured with the cube photometer by employing colour filters at position F. The photometer is calibrated by measuring the intensity of light when the face AD is partly covered with squares of paper of known area blacked with carbon black, but with the use of a different colour filter (red, green and blue) for each series and plotting a curve for each showing the value of $\left(\frac{d_1}{d_2}\right)^2$ against the percentage of total whiteness for each colour.

The article is printed on two kinds of white paper of two tints, of which the per cent. brightness and percentages of excess red and excess blue are given in order to illustrate the measurements described.

R. F. I.

A Laboratory Ozoniser. A. L. Henne. (*J. Amer. Chem. Soc.*, 1929, **51**, 2676–2677.)—An inexpensive apparatus is described which is a simplification of the ozoniser described by L. I. Smith (*J. Amer. Chem. Soc.*, 1925, **47**, 1844). The figure, which shows one of the ozone tubes, is self-explanatory. A lead wire dipping in dilute sulphuric acid is used as one of the electrodes; the lead wire (six fuse-wires twisted together) remains straight and centred by virtue of its own weight, so that sparking is prevented. As in the apparatus of Smith, three tubes



are sealed in series, and almost completely immersed in a bath of water in a battery jar. The water is used as a second electrode and as a cooling medium. No mercury is used, and the weight of the tubes is nearly counterbalanced by the weight of the water displaced; therefore, to maintain the tubes in position a plate of bakelite is blocked 3 cm. from the bottom of the battery jar, and fitted with slots to hold the lower extremities of the tubes, and the lid of the battery jar is fitted with corresponding slots (except that the diameter of the holes is 4 cms. instead of 3.5 cms.). The tension (10,000 v.) between the electrodes is furnished by a $\frac{1}{4}$ -kw. transformer. Complete drying of the oxygen is very important. The yield of ozone is substantially the same as that indicated by Smith; the percentage weight of ozone is about 14 per cent., 8 per cent. and 3 per cent. when oxygen is delivered at the rate of 4, 20 and 100 litres per hour, respectively. This corresponds to an hourly output of 0.7, 3.6 and 4.6 grms. of ozone. With this apparatus the oxidation of double linkages by means of ozone is exceedingly simple.

P. H. P.

References to Scientific Articles not Abstracted.

THE NATURE OF THE COLOUR OF POTTERY, WITH SPECIAL REFERENCE TO THAT OF ANCIENT EGYPT. By A. LUCAS. *J. Roy. Anthropol. Inst.*, 1929, 69, 113-129.

Red pottery—Gray and drab pottery—White pottery—Black pottery—Red and black pottery—Oxides of iron and their preparation—Deductions as to the preparation and composition of Ancient Egyptian pottery.

SILICA IN MINERAL WATERS. By P. HEFFERMAN. *Arch. Med. Hydrology*, 1929 (May).

Silica in thermal spa waters is mainly a colloidal hydrosol—In this state it cannot be determined in terms of silica or silicon ions—Activities of such spa waters are (a) adsorptive and (b) coagulant—They depend upon the "selectivity" of the colloid.

PHOTOMICROGRAPHS OF PHILIPPINE STARCHES. By R. N. ALLEN.

Forty-five photomicrographs, with descriptions, of starches from different kinds of Philippine tubers—Kamote (sweet potato)—Biga—Úbi (yam)—Tugi (yam)—Lima-lima (yam)—Aroro (arrowroot)—Kamoting-kahoy (cassava).

Reviews.

HYDROGEN IONS. THEIR DETERMINATION AND IMPORTANCE IN PURE AND INDUSTRIAL CHEMISTRY. By HUBERT T. S. BRITTON, D.Sc., etc. Pp. 515. Chapman & Hall. 1929. 25s. 0d.

During recent years many attempts have been made to correlate the hydrogen-ion concentration of a system with its physical, chemical or even physiological behaviour. In some cases, no doubt, the connexion was rather forced, and the over-estimation of the importance of these ions may have justified, to some extent at least, a well-known sceptic in calling them Hydrogen Ions! But at the same time it cannot be denied that a study of hydrogen-ion concentrations has thrown a considerable amount of light on many reactions both of analytical and of technical importance, with the result that analytical chemistry and industry have benefited to a valuable extent. Naturally the interest in the subject thus aroused has brought forth a certain amount of literature, but this has dealt more with the theoretical side, and there has hitherto been no reasonably comprehensive account of the practical aspects of hydrogen-ion concentrations.

In the book under review Dr. Britton has "endeavoured . . . to provide a practical discussion of the . . . methods of determining the concentration of hydrogen-ions, . . . to show their fundamental importance in general chemistry, including . . . analytical procedures; and . . . to indicate the important rôles played by hydrogen-ion concentrations in numerous industrial technical processes." There is no doubt that Dr. Britton has attained his objectives, and has made a valuable contribution to the literature of hydrogen ions. The first fourteen chapters of the book deal with the theory and practice of the methods of determining hydrogen-ion concentrations, including the "principles of volumetric analysis," then follow four chapters on the precipitation of hydroxides and basic salts. The last sixteen chapters are devoted to a discussion of the importance of hydrogen-ion concentrations in various industrial processes, *viz.* electro-deposition of metals; leather, sugar and paper manufacture; milk, brewing and baking industries; ceramics; etc. This latter part of the book will probably prove the most valuable, as the material contained in it has been collected from a large number of sources difficult of access. Dr. Britton does not deal separately with the subject of enzymes, although one might have expected such a treatment in view of the important contributions of Sørensen and his co-workers; various enzymes are, however, discussed in connection with technical processes.

It may, perhaps, be regarded as carping to criticise such an excellent book, but two or three points cannot be passed over. In the first place, the author does not appear to realise (p. 39) that the methods of determining P_H almost invariably gives a measure of the hydrogen-ion *activity* and not the concentration; the P_H scale as ordinarily used is, therefore, really an activity scale. Several

pages are devoted to the Ostwald theory of indicators but, as Dr. Britton points out, this is inadequate to account for their chemical properties; an important equation is deduced, however, on the basis of this discarded theory, and the point is not emphasised that the same equation can be deduced from the more complete modern theory. In the opinion of the reviewer the one-sided criticism of Werner's theory is somewhat out of place in a book of this type. The bi-valency of the mercurous-ion was established over thirty years ago by Ogg, and hence it is somewhat disappointing to find it still written as Hg^+ instead of Hg_2^{2+} .

Although the publishers have done their work quite satisfactorily, and the book is well produced, a number of misprints have been noted; but the difficulty of proof-reading the book must have been very great. In spite of the criticisms mentioned above this book may be warmly recommended to all who are interested in the subject of hydrogen ions.

S. GLASSTONE.

BACTERIOLOGY. By FRED WILBUR TANNER. Pp. xvii+548. Chapman & Hall. 1929. Price 22s. 6d. net.

As the author says in his preface, this book has been planned for those who are studying microbiology for the first time. His endeavour has been to present the whole field of bacteriological science to the reader without unduly emphasising any particular aspect, and especially without unduly emphasising the medical aspect. Moreover, his object throughout is not only to teach but to stimulate thought, and in this he has achieved considerable success, for the book is eminently thoughtful.

The scope of the book is very large, and includes the following topics:—History, Systematic Relationship; The Cell; Morphology; Chemical Composition; Classification; The Moulds; Yeasts; Protozoa; Action of Physical Agents; Relation of Chemical Agents (Disinfection); Mutual Relationship (Symbiosis, etc.); Nutrition; Growth; Enzymes; Nitrogen, Sulphur and Carbon Metabolism; Bacteriology of Air, Water, Sewage, Milk, and Dairy Products; Industrial Fermentation; Food Preservation; Illness caused by Foods; Relation of Bacteria to Disease; Transmission of Infection; Factors Influencing Infection; Modes of Bacterial Action; Protective Substances—Immune Bodies; Theories of Immunity; Varieties of Immunity; Bacteria in Plant Diseases; and Appendix, containing topical outlines for lectures and discussions, a list of publications in bacteriological literature and other useful matter.

It is obvious that with so large a scope no great detail can be expected; nevertheless, when occasion demands, the author goes into considerable detail, as, for example, when he devotes three whole pages to the exposure of the fallacious term "ptomaine poisoning." The book contains a surprising amount of useful information, such as the instructions from the Illinois Department of Public Health

for the sterilisation of water on a small scale with chloride of lime, a good description of the food-canning industry, a good account of botulism and precautions to be taken (four simple expedients) to guard against poisoning by *B. botulinus* from canned foods. One is pleased to see that the excretal and non-excretal types of *B. coli* are distinguished and tests given for their differentiation.

In the chapter entitled Relation of Bacteria to Disease a very useful summary of the characteristics of some twenty common diseases is given. The chapter on Factors influencing infection is good, the rôle of vitamins in maintaining resistance to infection receives attention, and in the paragraph on furunculoses the old-fashioned treatment by poulticing is given the condemnation it deserves.

The section on Food-borne Infections is very disappointing, except as regards botulism. Following the old erroneous German school, the author fails to distinguish *Salmonella Schottmülleri* (*B. paratyphosus B.*) from *Salmonella Aertrycke* or from *Salmonella Suipestifer*, though in the references given at the end of the chapter he gives Savages' "Food Poisoning and Food Infections" and Jordan's "Food Poisoning." In the past American bacteriologists have completely disregarded the classical English work on this important subject, but for several years now Jordan, and for a year or two Meyer, the leading American authorities on food poisoning, have recognised the correctness and importance of these distinctions.

Professor Tanner possesses a very pleasing and lucid style, and is to be congratulated on producing an excellent text-book on bacteriology, not only suitable for beginners, but also of considerable interest for more advanced students. The publishers are also to be congratulated on their part; the book is well printed and very free from printers' errors.

D. R. WOOD.

THE PYROLYSIS OF CARBON COMPOUNDS. By CHARLES DEWITT HURD. American Chemical Society Monograph No. 50. Pp. 807. The Chemical Catalog Company, Inc., New York. 1929. Price \$12.50.

This book is one of the numerous works issued in recent years by the American Chemical Society in the series which aims at producing a number of volumes, each of which shall be a complete book of reference for some particular subject. In compiling "The Pyrolysis of Carbon Compounds" the author has followed the general scheme of the series. He has with great thoroughness ransacked the monumental works of Beilstein and Richter, and made free use of the journals and abstracts issued by the various chemical societies of the world. In this way he has gathered together a large number of facts which may be classed under the heading of the action of heat on carbon compounds. With consummate skill he has welded his data into a very interesting, although somewhat bulky, volume. The term "Pyrolysis" is used to cover any chemical change brought

about by heat. Thus, in addition to mere decomposition, he includes polymerisation and its converse, isomeric change, etc., but purely catalytic effects are omitted as being beyond the scope of the work.

The book opens with a chapter on generalisations which have emerged from a survey of the literature. Under this heading the rules of Least Molecular Deformation, of Bredt and of Blanc, Nèfs' Theory and the Principles of Electronic Attraction are stated. Each of these is illustrated by numerous examples, and is discussed in a critical spirit.

The remainder of the book is divided into sections under the headings of the various types of organic compounds. The following is a random selection of the subjects dealt with:—Aliphatic hydrocarbons, cyclic hydrocarbons, petroleum, rubber and related hydrocarbons, amides, anilides, hydrazides, and amino acids. Each of the subjects dealt with is amply illustrated and, where possible, generalisations are drawn.

From the nature of such a book easy reading is not to be expected, yet the author has succeeded in making his work very acceptable. Now and again the reader comes across some very interesting or suggestive fact. Thus due mention is made of Faraday's little-known contribution to the chemistry of rubber—so far back as 1826 (when he was working out the laws of electrolysis) he determined correctly the composition of caoutchouc ($C_{10}H_{16}$); and Klason's work on "the distillation of wood in a cathode light vacuum" suggests that fruitful research might be prosecuted by dealing with other organic "pyrolyses" at extremely low pressures. Or again, mention of Neuberg's interesting experiments in connection with the origin of petroleum, in which he heated together oleic and valeric acids and obtained an optically active product which gave the cholesterol test, assuredly suggests matter for further research. Similar instances, too numerous to mention, occur throughout the text.

There is very little in the book which is likely to call forth any adverse criticism, but the statements (p. 742) in the paragraph concerning Chinese wood oil (tung oil) are not in accordance with Böeseke's work on elaeostearic (elaemargaric) acid (*Rec. Trav. Chim. Pays-Bas*, 1927, 46; cf. also *ANALYST*, 1928, 53, 54, 75).

In comparison with the vast mass of well-written and interesting material contained in this book, the minor error mentioned above is of little importance. The author is to be congratulated on the able manner in which he has dealt with a very difficult and hitherto scattered subject. He has produced a rare thing—a readable reference book. The extent to which it is a reference book can be gauged by the fact that it contains two indexes (subject and author) covering 52 pages and, at a guess, considerably more than 3000 references to original memoirs. The other features of outstanding merit can be judged only by actual reading. In short, "The Pyrolysis of Carbon Compounds" is well worth the attention of all those interested in organic chemistry.

HAROLD TOMS.

RECENT ADVANCES IN HAEMATOLOGY. By A. PINEY, M.D. Second edition. Pp. x+318. London: J. & A. Churchill. Price 12s. 6d. net.

The pathologist of fifty years ago was a master of all branches of his subject. With the growth of knowledge in recent years specialisation has been inevitable, and morbid anatomists have become separated from bacteriologists and biochemists. In this book Prof. Piney has followed the modern tendency and limited its scope to the purely morphological aspect of haematology, and has omitted serology and chemistry entirely. In no other book of its size, however, is there anything giving so good a description of the morbid anatomy and histology of the blood and blood-forming organs.

After a discussion of the development of blood cells, the various blood diseases are described in detail. The changes found in the blood in various other diseases are shortly described, and finally five chapters are devoted to a consideration of various forms of splenomegaly. Three valuable appendices complete the book. The first is devoted to technique, and is an extremely useful chapter. Instead of describing numerous methods the author only describes the one he uses himself for each particular examination. In this way in a dozen pages we have a full description of all essential haematological processes instead of a brief mention of numerous alternatives. The second appendix gives a list of text-books and monographs for further study. They are chiefly German, and although "only books reposing on my own shelves have been included," they number over 100, and should be sufficient for anyone to start with. The third appendix is a glossary of terms, a most necessary part of any book on haematology, with its enormous nomenclature.

From cover to cover the book expresses the personal opinions of the author, and is entirely different from so many American monographs, which seem to be prepared by the "scissors and paste" method without any attempt at digesting the fragments. This, of course, has the disadvantage of personal bias, and also that certain aspects of the subject are barely mentioned; for example, the work of Price Jones on the size of red blood cells and the methods of Pijper and others for measuring them by the halometer. Nevertheless, the fact that it has had a second edition within a year of the first is sufficient evidence that the book has filled a gap in haematological literature, and it can be warmly recommended as a useful text-book.

W. D. NEWCOMB.

VOLUMETRIC ANALYSIS. Vol. II. PRACTICAL VOLUMETRIC ANALYSIS. By I. M. KOLTHOFF, with the collaboration of H. MENZEL. Authorised translation from the German by N. H. FURMAN. Chapman & Hall. Pp. 552. Price 25s.

This book completes the translation into English of Kolthoff's important work on Volumetric Analysis; the German original of this section of the work has

already been reviewed and a summary of its contents given (*ANALYST*, 1929, 257). The translation contains some fifty additional pages, supplied by Kolthoff, of new matter dealing with methods which have been devised and improved since the book was first written; the new material includes a chapter on the use of ceric sulphate as a volumetric reagent. When describing the German original the reviewer stated that this book was not for the beginner in volumetric analysis, and it would be as well to emphasise the fact once more; the book, however, contains an excellent critical survey of a large number of interesting methods, and a study of the work should well repay even an experienced analyst.

The English translation of Volume II suffers from the same defects as does that of the first volume (see *ANALYST*, 1929, 194); Dr. Furman has attempted a too literal rendering of the German, and consequently, as well as for other reasons, the English style has suffered. On page 98 is found the statement "we . . . have arrived at somewhat different results than Incze," and on page 299 we read, "Also in acetic acid solution at boiling, thiosulphate is only incompletely oxidised, even in a long time, according to Hönig and Zatzek." Apart from the occasional "roughness" of the English, the translation has been well done, and the work is singularly free from misprints; the most serious error noted was "hypochloric" for "hypochlorous" acid (page 311).

It should be mentioned that the normal potentials for chlorine, bromine and iodine, quoted on page 385 (also on page 370 of the German edition) are incorrect, although their order, which is really the important point, is correct. Curiously enough, the values for these electrode potentials are given correctly at the end of Volume I of this work.

S. GLASSTONE.

Publications Received.

- LAW AND INDUSTRY.** By G. S. W. MARLOW, B.Sc. F.I.C. London: Baillière, Tindall & Cox. Price 18s.
- GASEOUS COMBUSTION AT HIGH PRESSURES.** By W. A. BONE, D.Sc., F.R.S., D. M. NEWITT, Ph.D., and D. T. TOWNEND, Ph.D. London: Longmans, Green & Co. Price 42s. net.
- A TEXT-BOOK OF BIOCHEMISTRY.** By A. T. CAMERON, D.Sc., F.I.C. 2nd Edition. London: J. & A. Churchill. Price 15s.
- CHEMISTRY IN DAILY LIFE.** By S. GLASSTONE, D.Sc., F.I.C. London: Methuen & Co. Price 6s. net.