THE ANALYST

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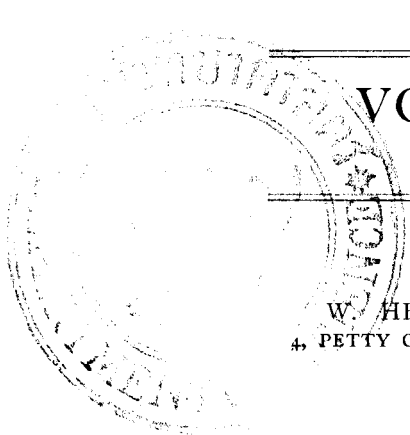

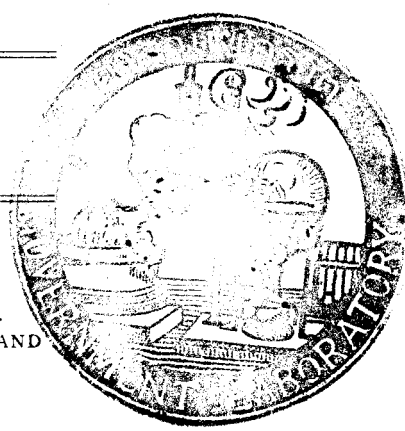

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THE ANALYST

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

AN Ordinary Meeting of the Society was held on Wednesday, December 5th, at the Chemical Society's Rooms, Burlington House. The President, Mr. P. A. Ellis Richards, F.I.C., was in the chair.

Certificates were read for the first time in favour of:—Messrs. Frank Knowles, Archibald Knox, A.I.C., Charles Roger Middleton, B.Sc., A.R.C.Sc., D.I.C., A.I.C., Harold Richard Read, A.I.C., George Hogan, F.I.C., and Thomas Francis Doyle.

Certificates were read for the second time in favour of:—Messrs. Robert Charles Frederick and Hubert Thomas Stanley Britton, M.Sc. (Lond.), F.I.C.

The following were elected Members of the Society:—Messrs. Laurence Eversley Campbell, M.Sc. (Lond.), F.I.C., John Troubridge Hannen, B.A. (Cantab), A.R.C.Sc., A.I.C., Cyril Langley Hinton, F.I.C., Douglas William Kent-Jones, B.Sc. (Lond.), F.I.C., Thomas William Alan Shaw, M.Sc. (Liv.), William Hall Simmons, A.I.C., Kenneth Edward Nethercoate Williams, and Percy Noel Williams, M.Sc. (Liv.), A.I.C.

The following papers were read:—"Crystalline Bromides of Linseed Oil," by Harold Toms, M.Sc. (under the Analytical Investigation Scheme); "The Plea for Standardisation," by M. S. Salamon, B.Sc.; "Note on the Estimation of Chromium," by Hubert T. S. Britton, M.Sc., F.I.C.; and "The Colorimetric Estimation of Lead in Cream of Tartar," by R. L. Andrew.

The Application of the Iodimetric Method to the Analysis of Sugar Products.

By C. L. HINTON, F.I.C., and T. MACARA, F.I.C.

(*Read at the Meeting, October* 3, 1923.)

During the last few years the iodimetric process for the estimation of reducing sugars has been examined by a number of investigators, the chief of these being Willstätter and Schüdel (*Ber.*, 1918, **51**, 780; Analyst, 1918, **43**, 416); H. M. Judd (*Biochem. J.*, 1920, **14**, 255; Analyst, 1920, **45**, 224); Baker and Hulton (*Biochem. J.*, 1920, **14**, 754); and Cajori (*J. Biol. Chem.*, 1922, **54**, 617 ; Analyst, 1923, **48**, 73). (See also note at end.)

The process consists essentially in adding a known amount of standard iodine solution to a given quantity of the dilute sugar solution, rendering the mixture alkaline and allowing it to stand for a short time, then re-acidifying and titrating the excess of iodine with standard thiosulphate solution. In most cases, sodium hydroxide is used for making the solution alkaline, though Cajori prefers sodium carbonate, as being less likely itself to affect the sugars. As will be seen, quite definite results can be obtained with sodium hydroxide, and this has been used in the present experiments. A few experiments on the effect of other alkalis are, however, described at the end of this paper. The alkali should always be added after the mixing of the sugar and iodine solutions.

The whole series of operations is carried through quite rapidly, and with a minimum of apparatus and reagents which are readily available in any laboratory, so that the process recommends itself admirably for factory analysis. Unfortunately the statements as to the extent to which the different sugars are oxidised by the alkaline iodine solution are not altogether in agreement, and it was as an attempt to clear up these points and to place the iodimetric analysis of sugar mixtures on a sound basis, that the present work was carried out.

General Experimental Procedure.—The required amount of sugar solution was measured into a 250 c.c. conical flask, and made up to approximately 50 c.c. with distilled water; 40 c.c. of 0·05 *N* iodine solution were then added, followed by the required amount of 0·5 *N* sodium hydroxide solution, and the flask stoppered. After standing for the time required, the mixture was acidified with 5 c.c. of 2 *N* sulphuric acid and immediately titrated with 0·05 *N* thiosulphate solution, accurately standardised against pure potassium iodate. Starch was used for the end-point. In all cases one or more blank experiments, in which distilled water was used in place of the sugar solution, were carried out at the same time and under the same conditions as each series of experiments.

I. DEXTROSE.

Most observers find a quantitative oxidation of dextrose to gluconic acid by alkaline iodine, according to the equation:

$$C_6H_{12}O_6 + I_2 + 3NaOH = C_5H_{11}O_5COONa + 2NaI + 2H_2O.$$

1 grm. of dextrose should therefore require 1·410 grm. of iodine for oxidation.

Miss H. M. Judd, however, reports finding only 1·315 grm. iodine required per 1 grm. of dextrose, and concludes that the oxidation of dextrose is never complete, though a definite and constant weight of iodine always reacts with a given weight of dextrose.

A. PRELIMINARY EXPERIMENTS.—Some preliminary work, to fix the experimental conditions, was carried out on a sample of nearly pure commercial dextrose. This material gave the following analytical figures:—Moisture, 2·52 per cent.; $[\alpha]_D$ (15 per cent. concn.) +51·0°; $[\alpha]_D$ on dry basis = +52·3°.

(*a*) *Variation in Amount of Alkali Used.*—A 0·2 per cent. solution of the dextrose was prepared, and quantities of 40 c.c., made up to 50 c.c. before adding the iodine, were used for each titration. Varying quantities of 0·5 *N* soda were then added, the flasks stoppered, and the solutions allowed to stand at room temperature for 10 minutes; 5 c.c. of 2 *N* sulphuric acid were then added, and the solutions at once titrated.

The results are collected in Table I.

TABLE I.—EFFECT OF VARIATION IN AMOUNT OF ALKALI USED.

Amount of sugar in each titration:—0·08 grm.
Time of reaction:—10 minutes.
Blank titration:—39·13 c.c. of 0·05 *N* thiosulphate solution.

No.	Sodium hydroxide (0·5 *N*) solution. c.c.	Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
1	3	25·12	14·01	1·112
2	4	22·14	16·99	1·348
3	5	21·96	17·17	1·362
4	6	22·02	17·11	1·357
5	7	22·14	16·99	1·348
6	9	22·72	16·41	1·302
7	10	23·13	16·00	1·270

In No. 1 the amount of sodium hydroxide is obviously deficient. No. 3, where 5 c.c. of 0·5 *N* sodium hydroxide solution were used, gives the maximum iodine value for the sugar. In this case the ratio of iodine to sodium hydroxide in terms of normal concentrations is 1:1·25, and this amount of sodium hydroxide approximately corresponds to the amount necessary for the neutralisation of the

gluconic and hydriodic acids formed by oxidation of the sugar, with sufficient excess for the formation of hypoiodite with all the excess of iodine:

$$I_2 + 2NaOH = NaOI + NaI + H_2O.$$

Alkali in excess of this amount diminishes the apparent iodine value of the dextrose, just as does a deficiency. Even a ratio of 1:1·5, as shown by No. 4, shows a slightly low value, although this is the proportion usually recommended. This would theoretically be the amount of sodium hydroxide required if the whole of the iodine entered into the glucose reaction (given by first equation above), but as in practice at least half of the iodine is unattacked, a certain slight excess of alkali must be present if the ratio 1:1·5 is maintained.

(*b*) *Proportions of Dextrose to Iodine.*—In this series varying amounts of dextrose solution were measured out, made up to 50 c.c., and the iodine and sodium hydroxide added. The time of reaction was 10 minutes. For Nos. 1 to 5, 6 c.c. of sodium hydroxide solution were used; for the others, 5 c.c.

The results, given in Table II., show that, provided not more than about half of the total iodine is used up, the proportion of dextrose to iodine does not affect the result. Obviously, it is an advantage to work with as large a quantity of sugar as possible, whilst remaining within safe limits. A suitable amount would be 0·08 grm. dextrose for 40 c.c. of 0·05 *N* iodine.

TABLE II.—EFFECT OF VARYING EXCESS OF IODINE USED.

Time of reaction:—10 minutes.
Blank titration:—39·13 c.c. 0·05 *N* thiosulphate solution.

No.	Dextrose. Grm.	Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
6 c.c. of 0·5 *N* NaOH used.				
1	0·02	34·86	4·27	1·355
2	0·04	30·55	8·58	1·361
3	0·05	28·42	10·71	1·359
4	0·08	22·07	17·06	1·353
5	0·08	22·02	17·11	1·357
5 c.c. of 0·5 *N* NaOH used.				
6	0·08	21·96	17·17	1·362
7	0·10	17·78	21·35	1·355
8	0·12	13·95	25·18	1·332

(*c*) *Time of Reaction.*—Willstätter and Schüdel recommend that 12 to 20 minutes be allowed for the reaction to take place. Baker and Hulton state that 3 to 5 minutes suffice. From the experiments detailed in Table III., in which varying periods were used, it would appear that 5 minutes may be insufficient in the case of dextrose. There appears, however, to be no appreciable action after 10 minutes.

TABLE III.—EFFECT OF TIME OF REACTION.

Amount of sugar in each titration:—0·08 grm.
Blank titration:—39·13 c.c. of 0·05 *N* thiosulphate solution.

No.	Time.	Thiosulphate (0·05 *N*) solution. required. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
6 c.c. of 0·5 *N* NaOH.				
1	5 mins.	22·57	16·56	1·314
2	10 ,,	22·02	17·11	1·357
3	20 ,,	22·05	17·08	1·355
5 c.c. of 0·5 *N* NaOH.				
4	10 ,,	21·96	17·17	1·362
5	20 ,,	21·94	17·19	1·364

(*d*) *Concentration of Reacting Mixture.*—For this purpose a 0·8 per cent. solution of the dextrose was prepared, and in each case 10 c.c. were accurately measured out and made up with distilled water to the required volume. The results in Table IV. show slightly higher figures for Nos. 1, 2 and 5. This is probably due to slight loss of iodine by volatilisation, from these more concentrated mixtures. The total volume of reacting solutions should conveniently be about 100 c.c. per 40 c.c. of 0·05 *N* iodine used. Nos. 5, 6 and 7 are the results of an attempt to ascertain whether increasing the dilution of the solution had any effect on the influence of an excess of alkali in diminishing the iodine value; this does not appear to be the case.

TABLE IV.—EFFECT OF CONCENTRATION OF SOLUTION.

Amount of sugar in each titration:—0·08 grm.
Blank titration:—38·58 c.c.
Time of reaction:—10 minutes.

No.	Vol. of sugar solution. c.c.	Total vol. c.c.	Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
5 c.c. of 0·5 *N* NaOH.					
1	10	55	21·35	17·23	1·367
2	30	75	21·38	17·20	1·365
3	50	95	21·41	17·17	1·362
4	70	115	21·41	17·17	1·362
8 c.c. of 0·5 *N* NaOH.					
5	30	78	22·10	16·48	1·308
6	50	98	22·14	16·44	1·304
7	70	118	22·13	16·45	1·305

B. Iodine Reducing Power of Pure Dextrose.—The commercially pure dextrose used above was recrystallised from dilute alcohol, the first crop of crystals being rejected and only the middle crystallising portion of the sample being retained. This was washed on a Büchner funnel with 70 per cent. alcohol, absolute alcohol and ether, and dried initially at 45° C., with gradual raising of the temperature to 95° C. About 10 per cent. of the original dextrose was thus recovered, which gave the following figures on analysis:—Moisture (105° C.), 0·21 per cent.; ash, 0·07 per cent.; $[\alpha]_D^{20}$ const. (5 per cent. solution) +52·67° C.; on dry basis = +52·78° C.)

For the determination of the iodine value a 0·8 per cent. solution of this dextrose was prepared, and 10 c.c. accurately measured out and made up to 50 c.c. before adding the 40 c.c. iodine solution; 5 c.c. of 0·5 *N* sodium hydroxide solution were used, and the time of reaction was 10 minutes. The results are shown in Table V.; Nos. 2, 3 and 4 were carried out on a different solution and on a different occasion from No. 1. It will be seen that the average iodine reduction for this sample is 1·406 grms. per 1 grm. of sugar, which corresponds to a value of 1·410 grms. for dry ash-free dextrose. This is the theoretical value. The accuracy of a single determination appears to be about ±0·2 per cent.

TABLE V.—IODINE REDUCING POWER OF DEXTROSE.

Amount of sugar in each titration:—0·08 grm.
Amount of alkali in each titration:—5 c.c. of 0·5 *N* NaOH.
Time of reaction:—10 minutes.

No.	Blank titration. Thiosulphate (0·05 *N*) solution. c.c.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
1	39·50	21·79	17·71	1·405
2	39·21	21·45	17·76	1·409
3	,,	21·51	17·70	1·404
4	,,	21·47	17·74	1·407
			Average	1·406
			= on dry ash-free basis	1·410

In order to verify the experiments already carried out on the commercial dextrose as to the influence of varying excess of iodine, a series of titrations was carried out with the use of varying proportions of dextrose to iodine (Table VI.). Nos. 1 and 2 were made in the usual way outlined above; the others were done by

measuring out arbitrary quantities of dextrose solution, making the liquids up to 100 c.c. and using 40 c.c. of 0·1 *N* iodine solution and 10 c.c. of 0·5 *N* sodium hydroxide solution.

TABLE VI.—EFFECT OF VARYING EXCESS OF IODINE.

Nos. 1 and 2 carried out with 40 c.c. of 0·05 *N* iodine + 5 c.c. of 0·5 *N* NaOH.
Others with 40 c.c. of 0·1 *N* iodine + 10 c.c. of 0·5 *N* NaOH.
Time of reaction:—10 minutes.

No.	Dextrose. Grms.	Blank. Thiosulphate (0·05 *N*) solution. c.c.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
1	0·0500	39·38	28·31	11·07	1·405
2	0·0500	,,	28·30	11·08	1·406
3	0·05087	82·00	70·74	11·26	1·405
4	0·0846	,,	63·21	18·79	1·409
5	0·1245	,,	54·43	27·57	1·405
6	0·1472	,,	49·31	32·69	1·409
				Average	1·406(5)

Within the range of proportions used, there is no appreciable difference whether a smaller or larger amount of dextrose be taken. It must be noted, however, that in all these cases there is an excess of iodine greater than the total amount reduced. The average figure practically agrees with that of the previous series, with about the same degree of accuracy.

In view of the ease with which dextrose is quantitatively oxidised by alkaline iodine, it is difficult to account for Miss H. M. Judd's statement that the reaction is never complete.

II. LACTOSE.

A sample of pure milk sugar (lactose hydrate) was used, with the following analysis:—Moisture, 0·025 per cent.; ash, 0·065 per cent.; $[\alpha]_D^{20}$ (c = 5) + 52·3° C.

(*a*) *Variation in Amount of Alkali.*—A 0·4 per cent. solution was prepared, 40 c.c. being used for each titration, and made up to 50 c.c. before the iodine was added. Amounts of 0·5 *N* sodium hydroxide solution varying from 3 to 8 c.c. were used; the reaction time was 10 minutes. Table VII. shows that the maximum iodine consumption occurs when the ratio of iodine to sodium hydroxide is 1:1·13 to 1:1·25. In these cases the alkali is approximately the amount required for the neutralisation of the sugar acid and hydriodic acid found, and formation of hypoiodite with the excess of iodine, as was found in the case of dextrose.

TABLE VII.—LACTOSE. EFFECT OF VARYING PROPORTIONS OF ALKALI.

Amount of sugar in each titration:—0·16 grm.
Time of reaction:—10 minutes.

No.	Sodium hydroxide (0·05 *N*) solution. c.c.	Blank. Thiosulphate (0·05 *N*) solution. c.c.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
1	3	39·05	26·13	12·92	0·512
2	4	39·09	22·00	17·09	0·678
3	4·5	39·09	21·31	17·78	0·705
4	5	39·05	21·37	17·68	0·701
5	6	39·05	21·77	17·28	0·685
6	7	39·09	22·33	16·76	0·665
7	8	39·05	23·02	16·03	0·635

(*b*) *Proportions of Lactose to Iodine.*—Table VIII. shows the results for lactose when the proportion of sugar is varied, the iodine and alkali being kept constant. As with dextrose, there is no appreciable effect due to the amount of sugar, provided there is an excess of iodine at least equal to the amount reduced. In No. 5 the amount of iodine is obviously deficient. A convenient amount of lactose to use would appear to be 0·16 grm. per 40 c.c. of 0·05 *N* iodine.

TABLE VIII.—LACTOSE. EFFECT OF VARYING EXCESS OF IODINE.

Amount of alkali used:—5 c.c. of 0·5 *N* NaOH.
Time of reaction:—10 minutes.
Blank titration:—39·05 c.c. of 0·05 *N* thiosulphate solution.

No.	Sugar. Grms.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
1	0·04	34·63	4·42	0·701
2	0·08	30·16	8·89	0·704
3	0·10	27·98	11·07	0·703
4	0·16	21·39	17·66	0·701
5	0·20	17·69	21·36	0·678

(*c*) *Time of Reaction.*—The few experiments recorded in Table IX. show that with lactose, as with dextrose, 5 minutes appears to be rather insufficient for the completion of the reaction. On the other hand, No. 3 points to the possibility of a reduction of iodine beyond the theoretical value, if the time is prolonged; but the present experiments are perhaps inadequate to decide this point.

Lactose hydrate should have an iodine reducing power of 0·705 grm. of iodine per grm., corresponding to 0·743 grm. for anhydrous lactose. Miss H. M. Judd's figure of 1·502, and even that of Baker and Hulton (0·762), for anhydrous lactose, are higher than the figures found in these experiments, which show no reason for supposing that the theoretical figure does not hold good for the conditions arrived at here.

TABLE IX.—LACTOSE. EFFECT OF TIME OF REACTION.

Amount of sugar in each titration:—0·16 grm.
Amount of alkali:—5 c.c. of 0·5 *N* sodium hydroxide solution.
Blank titration:—39·09 c.c. of 0·05 *N* thiosulphate solution.

No.	Time.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
1	5 min.	21·57	17·52	0·695
2	10 ,,	21·41	17·68	0·701
3	20 ,,	21·22	17·87	0·709

III. SUCROSE.

There is some disagreement in the statements as to the behaviour of sucrose with alkaline iodine. Willstätter and Schüdel found no oxidation, whilst Miss Judd found 0·006 grm. of iodine reduced per 1 grm. of sucrose, and Baker and Hulton found 0·02 grm. per grm. of sucrose; both these figures were obtained, however, on amounts of 0·1 grm. of sucrose, and therefore with very small amounts of iodine taken up.

The sucrose used in the following experiments was a sample of pure sucrose supplied by Messrs. Tate for standardisation purposes. It contained 0·01 per cent. of moisture and 0·008 per cent. of ash, and polarised + 66·55° at 16° C., and at a concentration of 20 per cent.

(*a*) *Effect of Varying Proportions of Alkali.*—The sucrose was finely powdered and weighed out separately for each titration; it was dissolved in 50 c.c. of water, and the iodine and alkali added as usual. The time was kept at 10 minutes. As will be seen from Table X., the amount of alkali appeared to have little influence, even when as much as 20 grms. of sucrose was used.

TABLE X.—SUCROSE. EFFECT OF VARYING PROPORTIONS OF ALKALI.

Amount of sugar in each case:—20 grms.
Time of reaction:—10 minutes.
Blank titration:—38·90 c.c. of 0·05 *N* thiosulphate solution.

No.	0·5 *N* NaOH c.c.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grms.
1	3	31·96	6·94	0·0022
2	5	31·32	7·58	0·0024
3	8	30·78	8·12	0·0026

(*b*) *Effect of Varying Proportions of Sucrose to Iodine.*—Experiments in which different amounts of sucrose for the same amount of iodine were used showed that the iodine reduction is not strictly in proportion to the sucrose used. There

is a slight falling off with increasing amounts of sucrose, as Table XI. shows. This at once precludes the possibility of the reduction being due to traces of dextrose; for, if this were so, the reduction should be practically proportional to the sugar used.

TABLE XI.—SUCROSE. EFFECT OF VARYING PROPORTIONS OF SUCROSE TO IODINE (1).

Amount of alkali used:—6·5 c.c. of 0·5 *N* NaOH.
Time of reaction:—10 minutes.
Blank titration:—39·06 c.c. of 0·05 *N* thiosulphate solution.

No.	Sucrose. Grms.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sucrose. Grm.
1	2	37·83	1·23	0·0038
2	5	36·40	2·66	0·0034
3	10	34·18	4·88	0·0031
4	15	32·30	6·76	0·0029
5	20	30·42	8·64	0·0027

It appeared probable that the lower iodine reduction with the larger amounts of sucrose might be connected with the smaller excess of iodine. In order to examine this point, additions of 0·08 grm. of the dextrose used in Tables I. to IV. were made to two quantities of 4 and 8 grms. of sucrose. To allow sufficient iodine 50 c.c. of 0·05 *N* iodine solution were used in these cases, with 6·25 c.c. of 0·5 *N* sodium hydroxide solution. From the amounts of iodine reduced were deducted the amounts due to the dextrose, and the difference gave the iodine value of the sucrose used. (Table XII.) As anticipated, the figures were rather lower than when no dextrose was used, though not so low as might have been expected if the whole of the used-up iodine had been reduced by sucrose.

TABLE XII.—SUCROSE. EFFECT OF VARYING PROPORTION OF SUCROSE TO IODINE (2).

0·08 grm. commercially pure dextrose (Table I.) present in each case.
Iodine equiv.:—17·17 c.c. of 0·05 *N* iodine solution.
Amount of alkali used:—6·25 c.c. of 0·5 *N* NaOH.
Time 10 minutes. Blank titration, 49·38 c.c.

No.	Sucrose. Grms.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Less amount due to dextrose. c.c.	Iodine per 1 grm. of sucrose. Grm.
1	4	30·34	19·04	1·87	0·0030
2	8	28·83	20·55	3·38	0·0027

(*c*) *Effect of Temperature.*—Certain irregularities in the figures so far obtained for sucrose (*e.g.* compare Table X. with No. 4 of Table XI.) led to an investigation into the effect of temperature on the reaction, since it might be expected that here, dealing with a very incomplete oxidation, the temperature might considerably influence the extent to which the oxidation proceeded.

For this series the sucrose was dissolved in water and the temperature adjusted by means of a bath; the iodine and alkali were then added (at room temperature) and the mixture agitated in the bath for 3 minutes and allowed to stand in the bath for the remaining 7 minutes.

TABLE XIII.—SUCROSE. EFFECT OF TEMPERATURE.

Amount of sugar in each case:—20 grms.
Amount of alkali:—5 c.c. of 0·5 *N* NaOH.
Blank titration:—39·91 c.c. of 0·05 *N* thiosulphate solution.
Time:—10 minutes.

No.	Temperature. °C.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grm.
1	15	30·73	9·18	0·0029
2	22·5	25·42	14·49	0·0046
3	30	21·40	18·51	0·0059

The results (Table XIII.) showed a considerable increase of iodine reduction due to increased temperature; the iodine value at 30° C. was double that at 15° C., with an intermediate value at 22·5° C.

Accordingly, for further experiments on sucrose a standard temperature of 17·5° C. (the most suitable at the time this work was carried out) was adopted.

(*d*) *Effect of Time of Reaction.*—For the reason given in the preceding section, it might be expected that the reaction of sucrose with alkaline iodine would proceed much further when the time was prolonged. The point was investigated by allowing quantities of 10 grms. to react for increasing periods of 10 minutes, ½ hour, and 2 hours, with a blank in each case standing the same length of time. There was a rapid increase of reduction in the first half-hour, the rate of which, however, fell away considerably in the succeeding 1½ hours. A fourth mixture was then prepared and allowed to stand for 3 days at 17·5° C. There was no further increase, although the excess of iodine was considerable. The four experiments are recorded in Table XIV.; it appears that a maximum value for the iodine reduction is reached after about 2 hours, to the extent of 0·0067 grm. of iodine per 1 grm. of sugar.

TABLE XIV.—SUCROSE. EFFECT OF TIME OF REACTION.

Amount of sugar in each case:—10 grms.
Amount of alkali:—5 c.c. of 0·5 *N* NaOH.
Temperature:—17·5° C.

No.	Time.	Blank. Thiosulphate (0·05 *N*) solution. c.c.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grm.
1	10 mins.	40·16	35·17	4·99	0·0032
2	30 mins.	40·14	30·90	9·24	0·0059
3	2 hrs.	40·12	29·48	10·64	0·0067
4	3 days	40·14	29·63	10·51	0·0067

(*e*) *Iodine Reducing Power of Sucrose.*—From the data given in Tables X. to XIV., it is possible to obtain a value for the reducing power of sucrose under the conditions of the standard procedure. This procedure, as originally outlined, must now be modified in cases where sucrose is present, by the adoption of a standard temperature, say 17·5° C. At this temperature, the iodine reduction of 10 grms. of sucrose for 10 minutes in presence of 40 c.c. of 0·05 *N* iodine solution and 5 c.c. of 0·5 *N* sodium hydroxide solution is 0·0032 grm. per 1 grm. of sucrose. The figures of Tables X., XI. and XII. are rather lower than this; but these were obtained at room temperature which, although not taken at the time, was certainly lower than 17·5° C.

For practical purposes it will be a sufficiently close approximation to take the figure 0·003 for the iodine value of sucrose. The figure obviously only becomes of importance at all in analysis when the amount of sucrose is relatively large compared with those of the sugars which are completely oxidised.

IV. LÆVULOSE.

Most observers have reported no oxidation of lævulose by alkaline iodine, but Miss Judd and Baker and Hulton found values of 0·10 grm. of iodine per grm. of lævulose. If this figure is correct, it will obviously seriously affect any attempts at estimation of dextrose in presence of lævulose.

Miss Judd gives no data as to the lævulose used, merely stating that its purity was tested by the polarimeter. The sample used by Baker and Hulton is described as having been recrystallised from alcohol, having $[\alpha]_D = -88{\cdot}4$ and a reducing power with Fehling solution, calculated as lævulose, of 99 per cent. Inasmuch as the $[\alpha]_D^{20}$ of lævulose at a concentration of 10 per cent. is $-92{\cdot}9°$ C. (Vosburgh), it appears doubtful whether their sample could have been entirely free from dextrose.

For these experiments a sample of lævulose purchased as pure, and having $[\alpha]_D^{20} -85{\cdot}6°$ C. on dry basis, in 20 per cent. solution, was recrystallised by the method described by T. S. Harding (*J. Amer. Chem. Soc.*, 1922, **44**, 1755). The product from the second crystallisation had the following analysis:—Moisture, 0·4 per cent.; ash, 0·02 per cent.; $[\alpha]_D^{20}$ (20 per cent. solution), $-94{\cdot}1°$ C. (on dry basis). (Vosburgh's formula for this temperature and concentration requires $-94{\cdot}3°$ C.)

(*a*) *Effect of Varying Proportions of Alkali.*—The lævulose in these experiments was separately weighed out for each titration, and dissolved in 50 c.c. of water. From the results of Table XV. it appears that an excess of alkali causes a considerably increased oxidation of lævulose. This is to be expected in view of the readiness with which lævulose is attacked by alkalis. A few experiments were also carried out in which a small amount of dextrose was used in addition to

the lævulose; in this case 50 c.c. of 0·05 *N* iodine solution were used (see Table XVI.). From the amounts of iodine reduced were deducted the amounts required by the dextrose for the respective proportions of alkali used; the remainder was taken as being the iodine reduction of the lævulose. As before, excess of alkali caused an increase in the oxidation of the lævulose.

TABLE XV.—LÆVULOSE. EFFECT OF VARYING PROPORTIONS OF ALKALI (1).

Amount of lævulose in each case:—2 grms.
Time of reaction:—10 minutes.
Blank titration:—40·32 c.c. of 0·05 *N* thiosulphate solution.

No.	NaOH (0·5 *N*) solution. c.c.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugar. Grm.
1	4	38·27	2·05	0·0065
2	5	37·80	2·52	0·0070
3	8	36·43	3·89	0·0124

TABLE XVI.—LÆVULOSE. EFFECT OF VARYING PROPORTIONS OF ALKALI (2).

Amount of lævulose in each case:—5 grms.
0·08 grm. of the commercially pure dextrose (Table I.) also present.
Time:—10 minutes.
Blank titration:—49·95 c.c. of 0·05 *N* thiosulphate solution.

No.	NaOH (0·5 *N*) solution. c.c.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Less amount due to dextrose (Table I.). c.c.	Iodine per 1 grm. of lævulose. Grm.
1	5	30·41	19·54	2·55	0·0032
2	6·25	29·17	20·78	3·61	0·0046
3	8	28·48	21·47	4·41	0·0056

(*b*) *Effect of Temperature.*—Before proceeding further with the experiments on lævulose, the temperature effect was examined, as this also might be considerable, as with sucrose. Accordingly 1 grm. quantities of lævulose were treated by the standard method at temperatures of from 14·5° to 25° C., the same procedure being adopted as for sucrose. The temperature effect was even greater than for sucrose, the iodine value being trebled between these extremes (see Table XVII.). It was evidently necessary here also to fix a standard temperature, and 17·5° C. was therefore used for the further experiments.

TABLE XVII.—LÆVULOSE. EFFECT OF TEMPERATURE.

Amount of lævulose in each case:—1 grm.
Amount of alkali:—5 c.c. of 0·5 *N* NaOH.
Time:—10 minutes.
Blank titration:—39·31 c.c. of 0·05 *N* thiosulphate solution.

No.	Temp. ° C.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of lævulose. Grm.
1	14·5	38·23	1·08	0·0068
2	17·5	37·59	1·72	0·0109
3	19	37·26	2·05	0·0130
4	25	36·08	3·23	0·0205

(*c*) *Effect of Varying Proportions of Lævulose to Iodine.*—As with sucrose, the experiments designed to show the effect of increasing quantities of lævulose in proportion to iodine, showed a falling off in the iodine reduction as the amount of sugar was increased (Table XVIII.). (No. 4 of this series is included, although the temperature was not noted, as it was determined on a separate small quantity of lævulose which had been specially recrystallised from the original material. Its polarisation on the dry basis agreed with that required by Vosburgh's formula. The temperature was probably rather on the low side.) This decrease is most marked for smaller amounts of sugar, and there appears to be a tendency to approximate to a constant figure of about 0·0065.

TABLE XVIII.—LÆVULOSE. EFFECT OF VARYING PROPORTIONS OF LÆVULOSE TO IODINE (1).

Amount of alkali used:—5 c.c. of 0·5 *N* NaOH.
Time:—10 minutes.
Temp.:—17·5° C. (except in 4).
Blank titration:—39·31 c.c. of 0·05 *N* thiosulphate solution.

No.	Lævulose. Grms.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of lævulose. Grm.
1	0·16	38·86	0·45	0·018
2	1·0	37·59	1·72	0·0109
3	2·0	36·57	2·74	0·0087
4	2·58	37·22	2·94	0·0072
		(Blank 40·16)		
5	5·0	34·03	5·28	0·0067

If dextrose is also present in amount sufficient to reduce an appreciable quantity of the iodine, the oxidation of the lævulose is diminished. Table XIX. shows the results found for various quantities of lævulose when 0·06 grm. of dextrose was also present. Here again the falling off in reducing power becomes less marked as the amount of lævulose increases, and appears to tend to a constant value of about 0·004.

TABLE XIX.—LÆVULOSE. EFFECT OF VARYING PROPORTIONS OF LÆVULOSE TO IODINE (2).

Amount of pure dextrose (Table V.) present in each case:—0·06 grm.
Amount of alkali used:—5 c.c. of 0·5 *N* NaOH.
Time:—10 minutes.
Temperature:—17·5° C.
Blank titration:—38·68 c.c. of 0·05 *N* thiosulphate solution.

No.	Lævulose. Grms.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Less amount due to dextrose. c.c.	Iodine per 1 grm. of lævulose. Grm.
1	0	25·40	13·28	—	—
2	0·25	24·97	13·71	0·43	0·0109
3	0·5	24·77	13·91	0·63	0·0080
4	2	23·63	15·05	1·77	0·0056
5	3	23·07	15·61	2·33	0·0049

(*d*) *Effect of Time of Reaction.*—As with sucrose, time appears to be an important factor in the extent to which lævulose is oxidised. Two grms. quantities of lævulose were allowed to react for 10, 20 and 30 minutes, under the standard procedure. The iodine reduction, which stood at 0·0087 after 10 minutes, had increased to 0·0154 in 30 minutes, but with a steady falling off in rate, tending to a maximum of, perhaps, 0·02 (Table XX.).

TABLE XX.—LÆVULOSE. EFFECT OF TIME OF REACTION.

Amount of lævulose in each case:—2 grms.
Amount of alkali used:—5 c.c. of 0·5 *N* NaOH.
Temperature:—17·5° C.
Blank titration:—39·31 c.c. of 0·05 *N* thiosulphate solution.

No.	Time. Minutes.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) reduced. solution c.c.	Iodine per 1 grm. of lævulose. Grm.
1	10	36·57	2·74	0·0087
2	20	35·37	3·94	0·0125
3	30	34·45	4·86	0·0154

(*e*) *Iodine Value of Lævulose.*—Contrary to what is required in the case of sucrose, the point of analytical interest in connection with lævulose is its iodine value in small amounts, approximately equal to the amounts of dextrose likely to be titrated, since in analytical work this is by far the most frequent case. Sucrose, on the other hand, may occur in much greater quantity, and its effect has, therefore, been investigated over a wide range.

If the figures for lævulose in presence of dextrose (Table XIX.) be plotted as a curve, it is found that the iodine value when the lævulose is about 0·06 grm. is approximately 0·012. For solutions of invert sugar, etc., where about 0·12 grm. of invert sugar would be titrated per 40 c.c. of 0·05 *N* iodine solution, the effect of the lævulose on the iodine must be reckoned as 0·012 grm. of iodine per

1 grm. of lævulose. This is very much less than that noted by Miss Judd or by Baker and Hulton, but it is not altogether negligible. It is sufficient to cause errors amounting to nearly 1 per cent. in the dextrose if not taken into account.

V. INVERT SUGAR.

It now became of interest to examine how far the results established for dextrose and lævulose could be used for the analysis of mixtures containing invert sugar or, by suitable inversion procedure, sucrose. As shown above, the extent of oxidation of lævulose is modified by the presence of dextrose, and the only point of interest here is the behaviour when the amounts of the two sugars are approximately equal.

(*a*) *Iodine Value of Lævulose in Presence of an Equal Amount of Dextrose.*—By applying the method of extrapolation to the results for fairly large quantities of lævulose in presence of 0·06 grm. of dextrose (Table XIX.), it has already been shown that the iodine value of the lævulose when 0·06 grm. of this is present would be approximately 0·012. The apparent iodine value of the total sugar, therefore, would be

$$\frac{1{\cdot}410 + 0{\cdot}012}{2} = 0{\cdot}711.$$

In order to test this figure a solution containing 0·2 per cent. each of the pure recrystallised dextrose (previously dried) and lævulose was prepared and carefully measured out from a burette in a series of increasing quantities, containing from 0·04 to 0·16 grm. of mixed sugars. These solutions were titrated by the standard procedure, and the results obtained are given in Table XXI.

TABLE XXI.—INVERT SUGAR. IODINE VALUE OF MIXTURES OF EQUAL QUANTITIES OF DEXTROSE AND LÆVULOSE.

Amount of alkali in each case:—5 c.c. of 0·5 *N* NaOH.
Time:—10 minutes.
Temp.:—17·5° C.
Blank titration:—39·52 c.c. of 0·05 *N* thiosulphate solution.

No.	Dextrose. Grm.	Lævulose. Grm.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of mixed sugars. Grm.
1	0·0199	0·0199	35·05	4·47	0·712
2	0·0350	0·0350	31·67	7·85	0·712
3	0·0500	0·0500	28·32	11·20	0·711
4	0·0651	0·0651	24·98	14·54	0·709
5	0·0800	0·0800	21·73	17·79	0·706

The iodine value found for the mixed sugars was 0·712 for the smaller amounts, with a slight decrease with increasing amounts of sugar down to 0·706 for 0·16 grm. of sugars. Apparently the higher figures are due to the increase in the oxidation of lævulose as the dextrose diminishes. The rather low value for No. 5 may be due to a considerable diminution in the lævulose oxidation as the limit of excess of iodine is approached.

(*b*) *Iodine Value of Invert Sugar from Sucrose.*—A solution was next prepared by dissolving 1·900 grms. of the pure sucrose before used in 150 c.c. of water, adding 30 c.c. of 0·5 *N* hydrochloric acid, and boiling for 1 minute. The solution was then quickly cooled, almost neutralised with 0·5 *N* sodium hydroxide solution, and made up to 500 c.c. (See Bolton and Revis, *Fatty Foods*, p. 316.) A series of quantities was measured from a burette, as above, and titrated. A series of iodine values was obtained which were all about 0·010 higher than the corresponding value found for mixed lævulose and dextrose. (Compare Table XXII. with XXI.) Apart from this, the slight decrease from the lower to the higher amounts of sugar corresponds closely to that shown in Table XXI., and probably has the same explanation. The higher figures for this series suggested the possibility of the presence of substances of higher reducing power than the sugars, which could only be derived from the method of inverting the sucrose. In order to test this point, a solution of 0·2 grm. each of dextrose and lævulose was prepared and treated by the same method used for inverting the sucrose (boiling with acid for 1 minute, etc.) The solution was made up to 200 c.c., and measured portions titrated as before. The series (Table XXIII.) showed a gradation corresponding well with those of the previous series, and with indications of very slightly higher values than those of Table XXI., though not approaching those of Table XXII.

TABLE XXII.—INVERT SUGAR. IODINE VALUE OF INVERT SUGAR PREPARED BY BOILING SUCROSE SOLUTION WITH DILUTE ACID.

Standard procedure.
Blank titration:—39·52 c.c. of 0·05 *N* thiosulphate solution.

No.	Invert Sugar. Grm.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of invert sugar. Grm.
1	0·0404	34·92	4·60	0·723
2	0·0699	31·57	7·95	0·722
3	0·1001	28·15	11·37	0·721
4	0·1296	24·80	14·72	0·720
5	0·1600	21·46	18·06	0·716

TABLE XXIII.—INVERT SUGAR. IODINE VALUE OF MIXTURES OF EQUAL QUANTITIES OF DEXTROSE AND LÆVULOSE (AFTER BOILING WITH DILUTE HCl).

Standard procedure.
Blank titration:—39·50 c.c. of 0·05 *N* thiosulphate solution.

No.	Mixed sugar. Grm.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of sugars. Grm.
1	0·0402	34·98	4·52	0·714
2	0·0403	34·96	4·54	0·715
3	0·0397	35·03	4·47	0·715
4	0·0701	31·64	7·86	0·712
5	0·1002	28·26	11·24	0·712
6	0·1302	24·92	14·58	0·711
7	0·1599	21·68	17·82	0·707

(*c*) *Effect of Boiling Dilute Hydrochloric Acid on Invert Sugar Solutions.*—A more drastic treatment was then followed by dissolving 0·0801 grm. each of dextrose (dried) and lævulose in 150 c.c. of water, adding 30 c.c. of 0·5 *N* hydrochloric acid, and boiling for 45 minutes. The solution was cooled, neutralised, and the whole titrated by the standard procedure. The iodine consumption was 39·51 −21·11 =18·40 c.c. of 0·05 *N* solution. This gives 0·729 grm. of iodine per grm. of mixed sugars—a value considerably higher than those of Table XXI.

In a final experiment to emphasise this effect of boiling with acids, 0·76 grm. of sucrose was dissolved in 150 c.c. water, 30 c.c. of 0·5 *N* hydrochloric acid added, and the solution boiled for 2 hours, then cooled, neutralised, and made up to 200 c.c. Measured portions were titrated, with the results shown in Table XXIV. These figures point to the presence of considerable quantities of substances other than the sugars in this solution, the only alternative being the unlikely conversion of lævulose into dextrose. The latter possibility was disposed of by estimation of reducing sugar by copper reduction; this showed that only 94·8 per cent. of the original invert sugar remained.

Hence it appears certain that the boiling of invert sugar solutions with dilute hydrochloric acid, such as used for inversion of sucrose, results in the destruction of the hexoses, with formation of products which reduce alkaline iodine. Even boiling for so short a period as 1 minute is sufficient to produce an appreciable amount of these substances.

TABLE XXIV.—INVERT SUGAR. APPARENT IODINE VALUE OF INVERT SUGAR BOILED WITH DILUTE ACID FOR 2 HOURS.

Standard procedure.
Blank titration:—38·52 c.c. of 0·05 *N* thiosulphate solution.

No.	Invert sugar. Grms.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of invert sugar. Grm.
1	0·0402	33·51	5·01	0·791
2	0·0795	28·72	9·80	0·782
3	0·1202	23·85	14·67	0·774
4	0·1603	19·13	19·39	0·763

(*d*) *Conditions for Satisfactory Inversion of Sucrose Solutions.*—In order to eliminate the destructive effect of the acid as much as possible, an inversion at a much lower temperature was tried. Ten c.c. of approximately 7 *N* hydrochloric acid were added to 80 c.c. of the sugar solution, and the flask allowed to stand in an incubator at 36° C. for 4 hours. The flask was then cooled, the solution almost neutralised with dilute sodium hydroxide solution, and made up to 200 c.c. Measured portions gave the figures shown in Table XXV., which agree well with those of Table XXI. (Mixtures of dextrose and lævulose.)

TABLE XXV.—INVERT SUGAR. IODINE VALUE OF INVERT SUGAR PREPARED BY INVERSION AT 36° C.

Standard procedure.
Blank titration:—39·45 c.c. of 0·05 *N* thiosulphate solution.

No.	Invert sugar. Grms.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. of invert sugar. Grm.
1	0·0400	34·97	4·48	0·711
2	0·1000	28·23	11·22	0·712
3	0·1599	21·58	17·87	0·709

Since a four hours' inversion would be unsuitable for many analytical purposes, an attempt was made to quicken the process by carrying out the inversion at 60° C. for 10 minutes. This gives practically the procedure used in the neutral polarisation process (Jackson and Gillis, *Bureau of Standards, Scientific Paper*, No. 375), except that sodium hydroxide is used for neutralisation of the acid, instead of ammonia.

The results are recorded in Table XXVI., and are, within experimental limits, in agreement with those of the dextrose and lævulose mixtures. The low value for No. 4 again points to the fact that the limit of excess of iodine is being approached. Under these conditions of inversion, then, and using about 0·12 grm. of invert sugar per 40 c.c. of 0·05 *N* iodine solution, the iodine value of invert sugar appears to be 0·710, a value which is in close agreement with that anticipated from a consideration of the behaviour of the individual sugars in other than equal proportions.

TABLE XXVI.—INVERT SUGAR. IODINE VALUE OF INVERT SUGAR PREPARED BY INVERSION AT 60° C.

Standard procedure.
Blank titration:—38·53 c.c. of 0·05 *N* thiosulphate solution.

No.	Invert sugar. Grm.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per 1 grm. invert sugar. Grm.
1	0·0398	34·05	4·48	0·714
2	0·0802	29·52	9·01	0·713
3	0·1198	25·12	13·41	0·710
4	0·1603	20·76	17·77	0·704

VI. ESTIMATION OF SUCROSE BY THE IODIMETRIC PROCESS.

It has now been satisfactorily established that the iodine reduction of invert sugar formed from sucrose under satisfactory condition is 0·710 grm. of iodine per grm. of sugar; and that the sucrose before inversion has a value of 0·003. Hence an increase in iodine reduction of 0·707 ÷ 0·95 will be noted per grm. of

sucrose inverted. This gives a factor of 0·744 for calculating sucrose from the difference between "direct" and "invert" iodine reductions. In both titrations there should be present from 0·08 to 0·14 grm. of total iodine-reducing sugar, calculated as invert, for each 40 c.c. of 0·05 *N* iodine solution added.

VII. ESTIMATION OF INVERT SUGAR BY THE IODIMETRIC PROCESS.

From the experiments detailed above as to the effect of acid treatment on invert sugar solutions it will be evident that an accurate estimation of invert sugar iodimetrically is a difficult problem. In commercial and technical products containing invert sugar there may be varying quantities of the decomposition products affecting the iodine titration, and, unless the manner of preparation of the invert sugar is known, and a standard can be prepared under the same conditions (which is seldom the case), its estimation by this method may be by no means exact. Nevertheless, in the course of much work in this laboratory involving the analysis of invert sugar, sucrose mixtures, jams, etc., it has been found that the figures obtained under the standard conditions of the present report do give fairly satisfactory results for invert sugar. If any doubt is entertained as to the results being obtained for invert sugar in the routine examination of a particular class of product, an occasional check by the copper reduction method will at once show up any errors (as in the case of the experiments above, Table XXIV.).

VIII. THE USE OF WEAK ALKALIS IN PLACE OF SODIUM HYDROXIDE.

With a view to the elimination of the slight effects of lævulose and sucrose on the alkaline iodine solution, some experiments were carried out with weaker alkalis in place of the sodium hydroxide.

(*a*) *Sodium Bicarbonate.*—Ten c.c. of a 0·8 per cent. solution of the pure recrystallised dextrose were taken, diluted to about 50 c.c., and 40 c.c. of 0·05 *N* iodine solution added, followed by 10 c.c. of M/2 sodium hydrogen carbonate solution. The mixture was kept at 27·5° C. for 1 hour, and was then acidified and titrated. Only 10·41 c.c. of 0·05 *N* iodine solution had been consumed, corresponding to an iodine value for the dextrose of 0·826. Without further prolonging the time or raising the temperature to an inconvenient extent, it is evident that the complete oxidation of the dextrose could only be attained by using excessive amounts of the alkali, which for several reasons (*e.g.* effervescence upon neutralisation) might be objectionable.

(*b*) *Sodium Carbonate.*—Ten c.c. of a 0·8 per cent. solution of the dextrose were used, and treated with 40 c.c. of iodine solution and 5 or 10 c.c. of 0·5 *N*

sodium carbonate solution for half-hour periods at 17·5° C. and 27·5° C. The results are given below (Table XXVII.).

TABLE XXVII.—USE OF SODIUM CARBONATE AS ALKALI.

0·08 grm. dextrose in each case. Standing for ½ hour.

No.	Blank titration. Thiosulphate (0·05 *N*) solution. c.c.	Amount of 0·5 *N* sodium carbonate. c.c.	Temp. ° C.	Back titration. Thiosulphate (0·05 *N*) solution. c.c.	Iodine (0·05 *N*) solution reduced. c.c.	Iodine per grm. of dextrose. Grm.
1	39·30	5	27·5	26·73	12·57	0·997
2	39·30	10	27·5	21·64	17·66	1·401
3	39·30	10	17·5	21·95	17·35	1·376

These figures were sufficient to show that, with suitable conditions, a satisfactory result could probably be obtained for dextrose by the use of sodium carbonate.

Before proceeding further, however, it was thought advisable to determine to what extent the action on lævulose would take place. Two grms. of lævulose were dissolved, 40 c.c. of 0·05 *N* iodine solution and 10 c.c. of 0·5 *N* sodium carbonate solution added, and the mixture kept for ½ hour at 27·5° C. (corresponding to No. 2 of Table XXVII.); a blank was carried out at the same time. The difference between the back titrations amounted to 3·96 c.c. of 0·05 *N* thiosulphate solution, giving an iodine reduction of 0·013 grm. per 1 grm. of lævulose. Hence it appears that for the conditions likely to give a satisfactory result for dextrose, the iodine reduction of the lævulose is just as marked whether sodium carbonate or sodium hydroxide be the alkali used. Cajori used sodium carbonate to the extent of about 1 per cent. in the mixture, with room temperature of about 20° C., and obtained satisfactory results for dextrose. Such amounts of sodium carbonate, in view of the present experiments, might be expected to have an appreciable action on the lævulose. In Cajori's experiments, however, the lævulose used was insufficient to show any effect on the iodine reduction within the limits of experimental error.

There thus appeared to be no advantage in the use of sodium carbonate, and the necessity for a higher temperature or longer time of reaction placed it at a considerable disadvantage as compared with sodium hydroxide. Accordingly the investigation of its effects was not carried further.

(*c*) *Borax.*—A number of titrations were made, with the use of dextrose and iodine as before, in conjunction with 0·25 *N* borax solution. (The 0·5 *N* solution crystallised, and had to be diluted.) In the following summary of the iodine values obtained, the amount of alkali is expressed as 0·5 *N* solution:

TABLE XXVIII.—IODINE VALUES FOR DEXTROSE WITH BORAX AS ALKALI.

No.	Amount of borax (0·05 *N*) solution. c.c.	Time.	Temp. ° C.	Iodine value found.
1	5	10 mins.	17·5	0·475
2	5	2 hrs.	17·5	1·201
3	5	½ hr.	27·5	1·225
4	5	1 ,,	27·5	1·349
5	10	1 ,,	27·5	1·264
6	4	2 hrs.	27·5	1·365
7	6	2 ,,	27·5	1·395
8	7	2 ,,	27·5	1·380
9	10	2 ,,	27·5	1·350
10	6	20 mins.	50° C.	1·409

Here, again, a satisfactory result for dextrose can be obtained, but only by using a fairly high temperature or a sufficient length of time. It was observed that the blank estimations (made side by side with each dextrose titration) were not in close agreement at 27·5° C., differences amounting to as much as 0·2 c.c. being found, which was a much greater difference than any found at ordinary temperatures. This adds still further to the objections to the use of weak alkalis, such as borax, which require an elevated temperature for the reaction. The only justification for its use would seem to be the smallness of the effect on lævulose, 2 grms. of which after 1 hour at 27·5° C., with the use of 5 c.c. of 0·5 *N* borax solution, showed an iodine value of only 0·0005.

(*d*) *Mixed Borax and Sodium Hydroxide.*—A mixed 0·5 *N* solution of borax and sodium hydroxide was prepared, with 2 equivalents of borax to one of sodium hydroxide (*i.e.* 60·3 grms. borax and 6·7 grms. of sodium hydroxide per litre). This solution was tested as in the case of the borax alone.

TABLE XXIX.—IODINE VALUE OF DEXTROSE WITH THE USE OF MIXED BORAX AND SODIUM HYDROXIDE.

No.	Amount of alkali (0·5 *N*) solution. c.c.	Time. Hours.	Temp. ° C.	Iodine value found.
1	4	1	27·5	1·355
2	5	1	,,	1·380
3	6	1	,,	1·378
4	7	1	,,	1·369
5	5	2	,,	1·400

The complete oxidation could, no doubt, be obtained with this mixture, but there appears to be no advantage over the use of borax alone, and the effect on lævulose would probably be more pronounced.

SUMMARY.

(*a*) Certain discrepancies in the literature on the subject as to the reduction by sugars of iodine in alkaline solution have been explained.

(*b*) The effects of proportions of iodine and of alkali used, and of time and temperature, in the cases of dextrose, lactose, sucrose, and lævulose have been examined.

(*c*) Dextrose and lactose are quantitatively oxidised to monobasic acids under suitable conditions. The action on sucrose and lævulose is small and very subject to the conditions of experiment, but, under definite conditions, these sugars exert a constant reducing power.

(*d*) A standard procedure has been outlined, which consists in using about 50 c.c. of solution containing about 0·08 grm. of dextrose or its equivalent, adding 40 c.c. of 0·05 *N* iodine solution and 5 c.c. of 0·5 *N* sodium hydroxide solution, and allowing the mixture to stand for 10 minutes at 17·5° C., then acidifying it with 5 c.c. of 2 *N* sulphuric acid, and at once titrating the excess iodine with 0·05 *N* thiosulphate solution.

(*e*) The iodine values found under these conditions are:

Dextrose	1·410 grms. iodine per 1 grm. sugar.
Lactose hydrate	0·705 „ „ „ „ „
Sucrose	0·003 „ „ „ „ „
Lævulose (in large amount)	0·0065 „ „ „ „ „
Lævulose (in presence of equal amounts of dextrose)	0·012 „ „ „ „ „

(*f*) Sucrose can be estimated by an iodine titration before and after inversion, with an accuracy of about 0·2 per cent., provided the inversion is carried out at a temperature not exceeding 60° C. The iodine value for sucrose is then 0·744.

(*g*) Invert sugar can be estimated in many products in the absence of lactose (and maltose) by a single titration with iodine, with sufficient accuracy for technical control purposes. The iodine value may be taken as 0·710.

(*h*) Weaker alkalis, such as sodium carbonate or borax, when used in place of sodium hydroxide, necessitate a much longer time of reaction or a higher temperature, and are therefore less suitable for use than sodium hydroxide.

(*Note.*—While the above work was being carried out, two papers have been published by I. M. Kolthoff (*Zeitsch. Untersuch. Nahr. Genüssm.*, 1923, **45**, 131, 141) on the iodimetric estimation of sugars. The conditions arrived at for the estimation of dextrose and lactose, with the use of sodium hydroxide for rendering the liquid alkaline, are very close to those found here. A few experiments on the reducing effect of sucrose and lævulose are described, and, so far as the results go, they are approximately in accordance with those of this report. The susceptibility of the reducing effect of lævulose to time, temperature, etc., is, however,

not worked out; consequently the conditions to be used in applying the suggested correction for the presence of lævulose in estimating the dextrose of invert sugar are inadequately defined.)

This investigation was carried out in the laboratories of the British Association of Research for the Cocoa, Chocolate, Sugar, Confectionery, and Jam Trades. The larger portion of the experimental work was done by J. R. Heather.

Discussion.

Mr. Charles M. Caines enquired whether the authors' method was applicable to the accurate estimation of small quantities of sugar in blood and similar biological material. He mentioned that at the meeting of the British Medical Association at Portsmouth he was demonstrating the method recommended by Dr. Maclean for the estimation of sugar in the blood in connection with the new insulin treatment. While listening to the author, it had struck him that if the process were capable of accurately estimating minute quantities of sugar it might afford a useful modification of the Maclean method, which, at present, depended on the reduction of alkaline copper iodine solution and involved a full six minutes' boiling.

Mr. A. E. Parkes enquired whether the authors' method could be applied to mixtures of sugars, such as lactose, invert sugar, and cane sugar in condensed milk, and glucose syrup, invert sugar and cane sugar in jams. After clarification with lead acetate, was it possible to obtain a solution which could be treated by the iodine process for the estimation of sugars?

Mr. C. L. Hinton, in reply, said the process was originally introduced by biochemists for the estimation of sugars in plants. He considered it might be equally useful for the estimation of sugar in physiological products, provided that proteins and other bodies which reacted with iodine were first removed.

As regards the question of its application to jams after clarification, they had found no difficulty in using the process for ordinary jams or for invert sugars and lactose, but glucose rather complicated matters. One could use the process in conjunction with polarisation, but, if lactose and glucose were both present, the estimation became more complicated, and it was necessary to use fermentation methods.

As regards sucrose, the accuracy was equal to that of the Fehling method, and the process was very much more rapid.

The Gold-Beater's Skin Test for Tannins.

BY PHYLLIS HONOR PRICE, B.Sc.

(*Read at the Meeting, November* 7, 1923.)

IN a recent communication from this laboratory (Atkinson and Hazleton, *Biochem. J.*, 1922, **16**, 516; ANALYST, 1923, **48**, 38) a qualitative test for tannins was described which is based on the fixation of the tannins on gold-beater's skin and the subsequent staining with ferric chloride. A specific test which demonstrates the " anning" properties of a tannin is of the greatest importance to the chemistry of the tannins, especially at a time when the syntheses of "tannins" have become the fashion, and I have therefore, at the suggestion of Dr. Nierenstein, attempted to increase the delicacy of the test, with the result that I have elaborated a method capable of detecting the "tanning" properties of 0·00005 grm. of gallotannin in 1 c.c. of water.

The gold-beater's skin test, as originally described by Atkinson and Hazleton, involves four distinct operations, namely (1) the swelling of the gold-beater's skin so as to make it permeable to the tannins; (2) the tanning of the gold-beater's skin; (3) the washing of the tanned gold-beater's skin so as to remove any tannin which had not been fixed; and (4) the staining of the tanned gold beater's skin with ferric chloride. I have studied all these operations separately, and, they are referred to in the present communication as *swelling*, *tanning*, *washing* and *staining*, respectively. It was also observed by Atkinson and Hazleton that the tanned and subsequently stained gold-beater's skin may be decolorised with dilute hydrochloric acid. I have used the latter process as a method for the detection of "phlobaphenes," and is referred to in this communication as *decolorising*.

SWELLING*.—Atkinson and Hazleton use water as a swelling reagent and, as the gold-beater's skin prepared according to their directions is frequently unevenly stained, I have tried other swelling reagents. I find an evenly stained specimen is always obtained if 2 per cent. hydrochloric acid is used for this purpose. As a comparison with 2 per cent. hydrochloric acid (about half-normal) the swelling properties of normal, half-normal and deci-normal solutions of sulphuric acid, acetic acid, succinic acid, formic acid, tartaric acid, and oxalic acid were also tried. None of these proved as effective as a 2 per cent. solution of hydrochloric acid. Similarly, stronger reagents such as for example, 5 per cent. hydrochloric acid, cannot be recommended as they, by themselves, darken the colour of the untanned gold-beater's skin and thus subsequently mar the staining effects produced by ferric chloride.

* These experiments were carried out in collaboration with Miss R. A. E. Colborn.

TANNING.—It must be noted that if hydrochloric acid is used as a swelling reagent it is very important to wash the gold-beater's skin carefully before tanning, as any hydrochloric acid, if present, affects the colour produced by ferric chloride. This is, of course, unnecessary when water is used as a swelling reagent.

Atkinson and Hazleton have fixed 30 minutes as the maximum time required for the tanning of the gold-beater's skin. I find that this suffices even for a solution of 0·00005 grm. of gallotannin in 1 c.c. of water.

WASHING.*—Atkinson and Hazleton have fixed the time required for the washing of the tanned gold-beater's skin as two minutes at a constant drip of two drops per second. From a large number of experiments I have come to the conclusion that the washing must be prolonged to 15 minutes, especially when ferrous sulphate and ferrous chloride are used as staining reagents. As will be seen later, these iron salts are far more sensitive than ferric chloride, and they were found to stain even gold-beater's skin which had been treated with gallic acid, if only washed for 2 minutes as recommended by Atkinson and Hazleton. This, however, is not the case if the washing is carried out for 15 minutes at a constant drip of 2 drops per second.

STAINING.—Numerous qualitative tannin tests have been recommended from time to time (compare, for example, Grasser, *Handbuch für Gerberei-Chemische Laboratorien*, 1922, pp. 241–273). I have, in addition to different iron-salts, also tested most of the heavy metals which have been suggested and several aniline dyes. In addition to this, I have tried the nitrous ether test of Vinson (*Botanical Gazette*, 1910, **49**, 222). All the reagents were at first tried on the untanned gold-beater's skin. Those which stained the skin without previous tanning were discarded. The following reagents were found to affect the untanned gold-beater's skin:

(1) Ferric oxalate.

(2) Silver nitrate, titanous chloride, titanic chloride, uranium acetate, gold chloride and thorium nitrate.

(3) The following aniline dyes:

Methyl violet, nigrosine, brilliant green, methyl green, Congo red, methylene violet, malachite green, methylene blue, crystal violet, Victoria blue, and cotton blue.

Hæmatoxylin was also tried and acted similarly.

A 1 per cent. solution of the staining materials was used, except in the case of the aniline dyes, which were 0·1 per cent. solutions.

In this connection it is interesting to note that the following substances, although recommended as specific reagents for tannins, had practically no effect on the tanned gold-beater's skin: Mercurous chloride, phosphotungstic acid and thallium chloride.

* These experiments were carried out in collaboration with Miss R. A. E. Colborn.

The iron-salts tested are herewith arranged according to their sensitiveness towards different gallotannin solutions, 1 per cent. solutions of the iron-salts being used:

Group I. *Sensitiveness*: 0·005 *per cent. gallotannin.*
Ferrous sulphate, ferrous chloride.

Group II. *Sensitiveness*: 0·01 *per cent. gallotannin.*
Ferric alum, ferric malate, ferric potassium tartrate, ferric sulphate, ferric ammonium chloride.

Group III. *Sensitiveness*: 0·02 *per cent. gallotannin.*
Ferric chloride.

Group IV. *Sensitiveness*: 0·05 *per cent gallotannin.*
Ferric perchloride, ferric acetate.

Group V. *Sensitiveness*: 0·1 *per cent. gallotannin and less.*
Ferrous ammonium sulphate, ferrous oxalate, ferric potassium oxalate, ferric succinate, ferric formate, ferric ammonium tartrate, ferric ammonium oxalate.

Mitchell's reagent (ANALYST, 1923, **48**, 2), which is a solution of 0·1 grm. of ferrous sulphate + 0·5 grm. of Rochelle salt in 100 c.c. of water was sensitive for 0·01 per cent. gallotannin and, consequently, can be grouped under II., although it contains less iron than the reagents given under Group II.

The heavy metals (1 per cent. solutions) used gave the following results:

Group I. *Sensitiveness*: 0·01 *per cent. gallotannin.*
Ammonium molybdate and vanadium chloride.

Group II. *Sensitiveness*: 0·05 *per cent. gallotannin.*
Potassium chromate.

Group III. *Sensitiveness*: *Less than* 0·1 *per cent. gallotannin.*
Copper sulphate.

As will be seen, the sensitiveness of these heavy metals is below that found for Group I. of the iron-salts.

Vinson's nitrous ether test gave very good results. Although amyl nitrite, when used on the gold-beater's skin in the same way as the other reagents, showed 0·01 per cent. gallotannin, it was possible to increase the sensitiveness to 0·005 per cent. by using the following technique:

The tanned skins were placed on paraffin-wax in a covered petri dish, which also contained a watch-glass with 1 c.c. of amyl nitrite. The solution being very volatile, the dish was soon filled with the fumes. No effect was observed until after about 20 minutes. Eventually, after repeated experiments, 3 hours was chosen as the time for the fumes to react, giving a deep brown-yellow coloration.

Similar experiments in which ethyl nitrite was used were found to detect only 0·1 per cent. of gallotannin.

In connection with all the experiments mentioned under staining it must be noted that control tests in which gallic acid was used were made in every case. None of them showed the slightest staining effect on gold-beater's skin treated with gallic acid.

DECOLORISING.*—Atkinson and Hazleton found that tanned and subsequently stained gold-beater's skin may be decolorised with 2 per cent. hydrochloric acid. I have obtained most satisfactory results when using 5 per cent. hydrochloric acid. In addition to this, I have also tested the decolorising effect of the following acids:

Oxalic acid—completely decolorised.
Tartaric acid—only very slightly decolorised.
Formic acid—not completely decolorised.
Succinic acid—not completely decolorised.
Sulphuric acid—completely decolorised.
Acetic acid—only very slightly decolorised.

During these experiments it was noticed that whereas pyrogallol tannins give a completely decolorised gold-beater's skin, on treatment with hydrochloric acid, catechol tannins leave an orange-brown stain on the skin, probably due to phlobaphenes. A series of experiments with a number of catechol tannins showed it to be a general reaction, and this was also confirmed by adding catechol tannins to pyrogallol tannins. I would therefore suggest that this method be used as a Test for Phlobaphenes.

GENERAL TECHNIQUE.—A small piece of gold-beater's skin, about ½ inch long and ¾ inch wide, is pinned on a flat surface of paraffin-wax, which is prepared by pouring melted paraffin-wax into a watch-glass.

1. *Swelling.* One c.c. of a 2 per cent. solution of hydrochloric acid is pipetted on to the skin and left standing for 10 minutes. The skin is then washed with distilled water at a constant drip of two drops per second for two minutes.

2. *Tanning.* The skin is treated with 1 c.c. of the solution to be investigated for the presence of tannin for 30 minutes. It is then washed as before for 15 minutes.

3. *Staining.* One c.c. of a 1 per cent. solution of either ferrous sulphate or ferrous chloride is left standing on the skin for 15 minutes and, as before, the skin is washed for two minutes.

4. *Decolorising when testing for phlobaphenes.* One c.c. of a 5 per cent. solution of hydrochloric acid is left on the skin for 2 minutes, and then the skin is washed, as before, for 2 minutes.

When dry, the skin may be mounted for reference and compared with skins treated with gallotannin solutions of varying concentrations. When very minute quantities indeed of tannins are suspected to be present, it is advisable to compare the skin also with untanned stained skins and stained skins which have been treated with gallic acid.

BIOCHEMICAL LABORATORY, CHEMICAL DEPARTMENT,
UNIVERSITY OF BRISTOL.

* These experiments were carried out in collaboration with Miss E. S. Smyth, B.Sc.

Discussion.

Mr. W. Partridge, mentioning a plant which he had sent to Mr. Mitchell in connection with the paper, said that tannins in land plants had more or less been investigated, but that water plants had been neglected in this respect. When approached on the matter he had happened to know one particular water plant—a species of *Potamogeton*—which contained tannin. This plant, which rotted in the water and produced an unpleasant smell, was found only in certain lakes; it had been observed that water taken from those lakes was quite inky, and, on investigation, it had seemed that this particular weed, in association with iron derived from ferruginous clay in the bed of the lake or from the iron pipes, was to blame.

Dr. H. E. Cox remarked that the difference between the specimen of untanned skin and one of the specimens of tanned skin seemed to be scarcely distinguishable by artificial light, and suggested that perhaps a greater difference was evident by daylight.

Mr. G. Rudd Thompson said he was much interested in the originality of the work done, but, referring to the manner of mounting the specimens, thought the colours would have been more easily compared if the specimens had been arranged so that one could look through the gold-beater's skin; by artificial light it was very difficult to see any appreciable difference in colour between the treated and untreated skin in the case of some of the specimens shown mounted on card.

Mr. W. T. Burgess pointed out that the pins used to hold the goldbeater's skin to the paraffin wax during treatment might affect the colour; he would like to have particulars of the pins used.

Mr. C. A. Mitchell, replying on behalf of the author, said he had tried the method, but could not say he was at all satisfied with the technique. In his opinion, the acid was liable to attack the pins and the wax was porous at the various perforations. In his experiments, therefore, he had fixed the skin between an ordinary microscope slide and a perforated one, held together by two screw clips, and had found this most satisfactory. It also enabled the treated skin to be examined by transmitted light. He had applied the test to a 5 per cent. extract of Mr. Partridge's pond weed, which gave a black coloration with ferric chloride on the skin.

The author's method of mounting her specimens gave a good colour by daylight. He had tried the effect of "osmic acid" as a staining reagent in the test, and had found it to give excellent results.

Mr. Rudd Thompson, referring to the arrangement with perforated slides devised by Mr. Mitchell for mounting his specimens, said that it might also be adopted with very favourable results in a microspectroscope; the cell made by fixing a short length of barometer tube to a plain slide often became detached in the middle of the operation.

The Corrosion of Aluminium Cooking Utensils.

BY C. KENNETH TINKLER, D.Sc., F.I.C., AND HELEN MASTERS, B.Sc.

IN the *Lancet* of January 4th, 1913, an account was given of some work carried out in the *Lancet* laboratory entitled "Some Kitchen Experiments with Aluminium." The general conclusion was reached "that any suspicion that aluminium may communicate poisonous qualities to food in the process of cooking may safely be dismissed."

Although, as a result of experiments carried out since 1913, there appears to be no reason to doubt the correctness of the above conclusion, yet in view of the greatly extended use of aluminium for cooking purposes, an account of some experiments we have made with aluminium cooking utensils may be of interest. Accounts of experiments of various other investigators on the corrosion of aluminium are to be found in the *Journal of the Institute of Metals.*

It is well known to those who make use of such vessels for cooking purposes that in certain cases extensive corrosion appears to have taken place, as indicated by the discoloration produced on the vessel. Thus when tap water is boiled in an aluminium saucepan a very dark stain is often produced, which is, however, much more pronounced in some cases than in others. The stain produced varies with the nature of the water and of the aluminium employed. Stains of different intensities are also often obtained with the same vessel and the same kind of water under different conditions of heating, and in some cases the stain may be partly masked owing to the deposition of calcium carbonate when hard water is boiled.

It is also apparently well known that this stain is removed if the vessel is subsequently used in an operation in which an acid liquid is employed, as for example in stewing fruit, and it can also be removed if a strongly alkaline liquid is heated in the vessel, or by means of an abrasive.

If water containing substances in solution or suspension is heated in an aluminium saucepan it is often found that the stain produced is much less pronounced than if water alone is heated in it. Thus if an egg is "boiled" in water in such a vessel a dark stain may be produced on the metal, whereas if the same vessel is used for "scrambling" an egg no stain is produced. It would be expected that if the egg were in any way connected with the apparent corrosion the attack would be more pronounced in the second case. Since, however, aluminium may be dissolved with or without blackening, it is impossible simply from the appearance of the saucepan to decide in which case greater corrosion has taken place.

THE NATURE OF THE DARK STAIN.—There is apparently no doubt that the dark stain is due to the presence of impurities in the aluminium, the chief of which is iron; and that by the action of an alkaline water an extremely small amount of

aluminium is removed from the surface, leaving behind the iron and other impurities which are insoluble in the alkaline water.

Iron is, of course, readily soluble in acid, so that the dark stain is removed by an acid liquid, and no stain is produced when commercial aluminium, which contains iron impurities, is being dissolved in acid.

We have compared the amount of iron removed from a stained and from a bright aluminium saucepan by treatment with very dilute sulphuric acid, and find approximately twice as much in the case of the stained pan.

In the case of one sample of commercial aluminium which showed pronounced blackening with tap water, an insoluble residue amounting to 2·2 per cent. of the material was obtained when the metal was dissolved in a solution of sodium hydroxide, this residue being a finely divided black powder, whilst for the same material the amount insoluble in hydrochloric acid was only 0·38 per cent. When such a sample of aluminium is dissolved in sodium hydroxide solution no dark film is observed as solution proceeds, although one may appear at first, as in this case probably owing to the rapid solution of the aluminium, the particles of iron become detached and remain suspended in the solution. This explains the removal of the dark stain by strong alkali.

For a given sample of aluminium and different samples of natural waters the intensity of the stain appears to depend in most cases, on the hydroxyl ion concentration of the water; the greater this concentration the darker the stain.

THE PROTECTION OF ALUMINIUM FROM CORROSION.—In view of the results obtained by Friend (*Trans. Chem. Soc.*, **1921**, **932**) on the protection of iron from corrosion in the presence of colloids, we carried out a number of experiments with reference to the protection of aluminium. There is apparently no doubt that the colloidal matter, which is frequently present when aluminium vessels are used for cooking food, materially lessens the amount of aluminium dissolved. Thus in one experiment the loss in weight of a disc of aluminium heated in a dilute solution of agar in tap water was only one-third of the loss in weight produced when the same disc was heated in tap water alone, and only very slight darkening was observed in the first experiment. The non-formation of a stain when an egg is "scrambled" in an aluminium saucepan may also be due to the presence of colloidal matter. Some results on the protection of aluminium by colloids are given by Friend (*loc. cit.*, **1922**, **468**.)

We have found that it is possible to prevent the discoloration of aluminium by tap water. If a solution of potassium dichromate is boiled in an aluminium saucepan no blackening takes place; in fact, aluminium so treated shows a slight gain in weight and is rendered "passive." Treatment with tap water does not now produce a stain. The effect, however, is not permanent.

To illustrate this action, a small quantity of a solution of dichromate is heated for some time in a bright aluminium saucepan, the pan is then washed out, filled with tap water and heated. A well-defined stain is obtained above the original level of the dichromate solution, but the part previously covered by the solution remains quite bright.

In connection with the cleaning of aluminium, reference should be made to a paper by Seligman and Williams (*J. Inst. Metals*, 1922, 297; ANALYST, 1922, **47**, 493). They find that the attack of an alkaline solution on aluminium is considerably retarded in the presence of sodium silicate, and that commercial preparations sold for cleaning the metal usually contain sufficient sodium silicate for this purpose.

CHEMICAL LABORATORY,
HOUSEHOLD AND SOCIAL SCIENCE DEPARTMENT,
KING'S COLLEGE FOR WOMEN, KENSINGTON, W.8.

Note.

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

THE ESTIMATION OF PHOSPHINE IN ACETYLENE.

IN estimating phosphine in acetylene generated from commercial calcium carbide the method of Lunge and Cererkreutz (as given by V. B. Lewes in *Acetylene*) was employed. The method is designed to give:—(1) The weight of acetylene evolved; (2) the amount of phosphorus absorbed by the wash solution (sodium hypochlorite); (3) the sulphur in the filtrate from (2) by precipitation as barium sulphate.

When the estimation was carried out as described by Lewes, with the use of granular calcium chloride to dry the gas prior to absorption, but with the substitution of four wash-bottles for the absorption bulbs, the following anomalous results were obtained:

(1) After clearing out the acetylene the last two wash-bottles smelt strongly of phosphine;

(2) The phosphorus recovered increased progressively in amount from the first to the last wash-bottle;

(3) Free sulphur was immediately precipitated in the first wash-bottle, but not in the succeeding bottles.

The sodium hypochlorite wash solution was prepared by the interaction of bleaching powder and sodium carbonate and made up to three per cent. NaOCl. A second solution was made by the method employed by L. M. Dennis and W. J. O'Brien (*J. Ind. Eng. Chem.*, 1912, 834), in which chlorine gas is passed into sodium hydroxide solution to saturation, excess of chlorine removed with a current of air, and the solution made up to 3 per cent. Both solutions gave identical results. The solutions were then tested by passing hydrogen containing phosphine through them, and it was observed that throughout the experiment the smell of phosphine persisted in the hydrogen issuing from the last bottles. The amount of phosphorus recovered again increased progressively in amount from the first to the last bottle of each series.

Another possible source of error is the use of calcium chloride in drying the acetylene, for, from an investigation by Stock, Böttcher and Lenger (*J. Chem. Soc.*, 1909, A ii, 727), it appears that inflammable P_2H_4 may be converted into the solid $P_{12}H_6$ by passing over granular calcium chloride, the solid $P_{12}H_6$ being retained by the chloride.

A modification of the combustion method was finally used. In order to avoid the use of oxygen and a special burner the acetylene was led either direct from the generator or from a gas-holder to an ordinary bicycle lamp acetylene burner. The flame was almost entirely enclosed in a glass hood connected directly with four wash-bottles containing slightly ammoniacal distilled water, and a rapid current of air was drawn through the system. By adjustment of the supply of acetylene the flame was prevented from smoking and the rate of the air current was such as to ensure complete withdrawal of the products of combustion. No oxygen supply was required. It was found that the phosphorus was retained almost wholly in the first wash-bottle, with a trace in the second and none in the third and fourth. The total recovered was nearly ten times as great as was obtained by the method of Lunge, though still within the limits for commercial acetylene as given by Lewes.

T. E. PERKS.

THE DOMINION LABORATORY,
WELLINGTON, 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 interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY BOROUGH OF SALFORD.

ANNUAL REPORT OF THE BOROUGH ANALYST FOR 1922.

THE total number of samples analysed was 1534,of which 1452 were taken under the Sale of Foods and Drugs Acts. Of these samples 82 (5·6 per cent.) were returned as adulterated, as compared with 8·7 per cent. in the previous year.

MILK.—Forty-nine of the 923 samples were adulterated. Of the 426 samples tested for dirt, 167 yielded no sediment; 59 gave 0·5 part, 117, 1· part; 4, 1·5 parts; 50, 3 parts; 6, from 4 to 5 parts; 14, 6 parts; 5, gave 9 parts; 2, 12 parts; and 2, 15 parts of dirt per 100,000. The lenient standard of a sediment not exceeding 5 parts per 100,000 has again been fixed as a maximum, and all milks giving a sediment in excess of that figure have been regarded as adulterated. The results obtained during the six years from 1915, however, indicate that a standard of not more than 1 part per 100,000 would be perfectly fair, and that milk containing 2 or more parts per 100,000 should be classified as unsatisfactory.

It is suggested that if the supply of milk of Grade "A" quality is so important that it is worth while having special legislation to ensure it, it would seem equally important to prevent the sale of grossly contaminated milk as ordinary milk.

MARGARINE.—It would seem that it was not the intention of the legislature that butter substitutes should be described as mixtures of butter and margarine, particularly in view of the definition of margarine in Sec. 13 of the Act of 1907 as "any article of food, whether mixed with butter or not, which resembles butter and is not milk-blended butter."

In view of these considerations proceedings were taken against four large firms for the improper labelling of margarine as mixed or blended with best butter.

Fines were inflicted in three cases, and the fourth was dismissed, as the word "margarine" was held to be the most conspicuous on the carton. As a result of

these prosecutions the slips inserted under the statutory wrappers, and the cartons, were withdrawn from all the branch shops of the firms throughout the country.

COCOA.—Fourteen samples were examined, of which 3 (prepared by one manufacturer) contained one-tenth grain of arsenic (expressed as arsenious oxide) per lb. The local manager of the firm was notified as to the result, and withdrew all stocks of cocoa which had been delivered to shops in the Borough prior to August 1, 1922.

CANNED GOODS.—All of the 20 samples of canned goods (6 of fish, 11 of fruit, and 3 of jam) contained small quantities of tin in solution when turned out of the can and thoroughly mixed. A sample of canned "Melon and Orange" jam contained 6 grains of metallic tin per lb. The vendor was interviewed and undertook to destroy the remainder of the stock, and the facts were communicated to the Authority in whose district were the premises of the wholesale dealer.

DRUGS.—Of the 116 samples examined, only three were adulterated. One of these, Epsom salts, contained 20 parts of arsenic per million, and the other two, borax, each contained 50 parts of arsenic per million. The vendors were notified, and at once withdrew their stocks.

PRESCRIPTIONS.—Fifty-one samples were taken, of which only 3 were unsatisfactory.

SODA WATER.—Two of 4 samples were found to be devoid of added sodium bicarbonate. The manufacturers agreed that "soda water" sold in Salford should actually be *soda* water. In 1919 the local Association of Mineral Water Manufacturers gave the opinion that soda water should contain 10 grains of sodium bicarbonate per pint. It is generally admitted that any quantity between 5 and 10 grains per pint is a suitable standard.

G. D. ELSDON.

Meteorological Office, Air Ministry.

ADVISORY COMMITTEE ON ATMOSPHERIC POLLUTION.

REPORT ON OBSERVATIONS IN THE YEAR ENDING MARCH 31ST, 1922.*

THE STANDARD GAUGE.—The results obtained for the amount of atmospheric pollution with 22 gauges operated by 12 authorities in different parts of the country are dissected out in tables, comparisons with averages for the corresponding months of previous years being made for the first time. Instead of the results being expressed, as previously, in metric tons per square kilometre, these figures have been multiplied by 100 to avoid decimal points, and therefore can be read as metric tons per 100 sq. kilometre, or as weight in grms. of deposit over a 10 metre square. In the mean monthly values for the whole year the most notable feature is the universally low rainfall, and the nearly universally low pollution average, probably directly connected with the restricted use of coal owing to the coal strike which lasted from April 1st to July 4th.

Tar was above the average at 3 out of the 8 London stations, Newcastle and Southport; Southwark Park, London, coming first, with 143 metric tons per 100 sq. kilometre, against an average for the previous 5 years of 35 metric tons.

Insoluble Carbonaceous Matter other than Tar was above the average at 3 London stations, Hull, Liverpool, Newcastle, Rothamstead, and Southport, the greatest deposit being in London (1043 m.t., with Newcastle next, 992 m.t.).

* M.O. 256. H.M. Stationery Office, Kingsway, W.C.2. Price 3s. net.

Insoluble Ash (*or dust*) was above the average at 4 London stations, Hull, Liverpool, Rothamstead and St. Helens, the greatest pollution again being in London (2138 m.t.), with Liverpool and Hull next (1600 and 1468 m.t. respectively).

Loss on Ignition (*volatile soluble compounds*) was only above the average at 2 stations, as was also the case with *Soluble Ash* (*non-volatile soluble compounds*).

Total Solids were greatest in London (3630 m.t.), and above the average in 3 stations.

The Total Deposit. On the average the summer total is less than the winter in 14 cases, equal in 3, and greater in 5, but in 1921–22 this was confirmed in only 8 cases, and contradicted by the relatively large deposits in 6 cases and low deposits at 2 stations.

A report by Dr. Ashworth on the *Deposits obtained at Rochdale* deals with the possible causes of the very high atmospheric deposit; with the seasonal variation shown by the total deposit; the close correspondence between the amount of soluble matter and rainfall; and the inverse relationship between the amounts of soluble and insoluble matter.

The Records of the Automatic Filter. Data for 4 stations, Kew Observatory, Richmond, Surrey; Savoy Hill, London; Westminster, London; and Rochdale, were available. In the case of the first 3 the results are treated on similar lines to those adopted in the 7th report (ANALYST, 1922, **47**, 256–258), the days being divided into summer and winter and the winter days into foggy (with a maximum shade number of 4 or over) and non-foggy. The days are further grouped into week-days (excluding Saturdays), Saturdays and Sundays. In considering the hourly distribution curves they are found on the whole to be very similar to those for previous years. In London on days without abnormal fog impurity begins to rise at 5 to 6 a.m.; attains a maximum at 10 a.m.; falls steadily till about 3 p.m.; rises slightly between 5 and 7 p.m.; and then falls, but on foggy days there is great delay in attaining the maximum. Taking the year as a whole, a slight improvement in the atmosphere is noted. The Rochdale figures show a very similar type of distribution. The effect of the coal strike is clearly seen from the records of the automatic filter. The graph for maximum suspended impurity for each day shows a steady fall from the end of April till at the end of September it begins to rise and fluctuate as usual.

ISOLATION AND EXAMINATION OF ATMOSPHERIC DUST BY THE JET APPARATUS. —This instrument (*cf.* ANALYST, 1922, **47**, 322), which was referred to in the 7th Report under the heading "November Fogs," has been further developed; it depends upon the fact that when air containing dust and a sufficiency of water vapour has its pressure suddenly reduced, condensation of the water takes place. This is brought about on a glass surface, and the moisture evaporated, leaving the adhering particles for examination. The whole apparatus is simple and can be purchased at the low price of £4 10s. 0d. The number of particles of dust per c.c. can be determined by means of this instrument; for example, during the dense fog of January 22nd, 1922, a record of 50 c.c. of air taken gave 21,750 particles per c.c., many having a diameter of 1·7 microns, and the average diameter being 0·85 microns. Expired air was also examined for dust particles by this instrument, and the method appears more sensitive than Tyndall's beam of light method. There are other indications of its usefulness in many directions, and work begun with it in connection with acidity and alkalinity has already shown promise.

Work on *Obscurity and Visibility* has not progressed very far during the year owing to difficulties of laboratory accommodation, but measurements on a uniformly illuminated area are expected to begin shortly.

D. G. H.

Fuel Research Board.

PHYSICAL AND CHEMICAL SURVEY OF THE NATIONAL COAL RESOURCES.

REPORT ON METHODS OF ANALYSIS OF COAL.*

THIS report describes in detail the proximate and ultimate analysis of coal, the estimation of phosphorus, caking-index, calorific power, carbon dioxide content, and gives a method for its high and low temperature assay. The important question of sampling is left over for a future report.

The following determinations are carried out on the air-dry sample ground to pass a No. 60 I.M.M. sieve. Moisture is estimated by heating 1 to 2 grms. in flat dishes in an oven at 105° to 110° C., and the ash is obtained by ignition in a muffle attaining a temperature of 750° to 800° C. For volatile matter 1 grm. is heated in a platinum crucible, having a diameter at the base of 24 to 25 mm., and height 35 to 40 mm., and provided with a well-fitting lid, to a temperature of 925°±25° C. for seven minutes. A muffle or an electric tube furnace is recommended, but an ordinary open flame may be used if it gives the required temperature, in which case the crucible is supported inside an asbestos-lined conical shield. In the ultimate analysis carbon and hydrogen are estimated in the ordinary way, with the use of lead and a silver spiral; carbon dioxide in the ash should be estimated and allowed for. Sulphur is estimated by ignition with magnesia (or lime), and sodium carbonate in the well known way, and for nitrogen the Kjeldahl method is recommended with the use of mercury or copper sulphate as accelerators, but it is admitted that such results are low. Phosphorus in the ash is precipitated by ammonium molybdate after treatment with *aqua regia*, evaporation of the solution to dryness, and fusion of the residue with sodium carbonate; the precipitate is either dried and weighed or treated with 0·1 *N* sodium hydroxide solution, the excess of which is titrated with 0·1 *N* nitric acid.

A modification of the Campredon test is used for determining the caking index. Twenty-five grms. of a mixture of coal and sand (which passes a No. 40 sieve and is retained by a No. 50) are heated exactly as in the estimation of volatile matter; the maximum proportion of sand which allows the coke to support a 500 grm. weight gives the caking index, but the proportion of loose powder in the crucible must not exceed 5 per cent.

In determining the calorific value, which is obtained by combustion in a bomb calorimeter, the usual precautions and corrections are detailed, including the correction for the acids formed.

A laboratory apparatus for the examination of coals by carbonisation at about 600° C. is described, which shows, with fair accuracy, the coke, gas, tar, liquor and ammonia yield which may be expected on the large scale. There are also tables showing the yields obtained from typical coals. For the quick determination of the carbonising characteristics Lessing's coking test is given (*cf.* ANALYST, **1912, 37,** 383), with the recommendation that it be used at 600° and 900° C. for comparative purposes.

A standardised form of report on a coal analysis is added, and an appendix quoting Sinnatt and Harrison's method for the estimation of carbon dioxide (*Lanc. and Cheshire Coal Res. Assoc., Bull.*, 7, 1920). H. E. C.

* Report No. 2. H.M. Stationery Office, London. 1923. Price 1s. 6d. net.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Analysis of the Jerusalem Artichoke. A. T. Shohl. (*J. Amer. Chem. Soc.*, 1923, **45**, 2754–2756.)—The following percentage composition of the edible portion of Jerusalem artichoke, *Helianthus tuberosus*, found by the author, agrees closely with the results of Strauss (*Berl. klin. Wochschr.*, 1912, **49**, 1213) and Langworthy (*U.S. Dept. Agr. Bull.*, 1917, **468**):—Moisture, 79·0; protein ($N \times 6{\cdot}25$), 3·1; true protein, 0·9; fat, 0·2; carbohydrate, 15·5; fibre, 0·8; and ash, 1·1 per cent. The carbohydrate was estimated by extracting the fresh vegetable or the air-dried material for 72 hours with boiling water. The extract was hydrolysed by refluxing for 2 hours with 10 per cent. of hydrochloric acid and the lævulose was estimated by Benedict's method (*J. Amer. Med. Assoc.*, 1911, **57**, 1193). The carbohydrate (inulin) content was 15·5 per cent. Of the total nitrogen, 71·5 per cent. was water-soluble, and hence not protein. Only small amounts of water-soluble vitamin *B* were present. Analysis, clinical experience and a single experiment in metabolism indicate that the Jerusalem artichoke is a valuable adjunct in the dietetic treatment of diabetes, and its use in this should be re-investigated.

P. H. P.

Estimation of Lipoids and Lipoid-Phosphoric Acid in Flours, Alimentary Pastes, and Eggs. R. Hertwig. (*J. Assoc. Off. Agr. Chem.*, 1923, **7**, 91–98.)—The term lipoids denotes the alcohol-ether extract and includes neutral fats, phosphatides, phytosterol, pigments, waxes and cerebrosides. To estimate lipoids in flour, etc., 10 grms. of the finely ground sample are mixed with 30 c.c. of 70 per cent. alcohol and heated at 75° C. for fifteen minutes; 55 c.c. of 95 per cent. alcohol are added, the mixture is shaken for two minutes, then treated with 75 c.c. of ether (dried over sodium), the shaking continued for five minutes, after which the mixture is submitted to centrifugal action and the clear liquid decanted. The residue is extracted with three successive portions of ether saturated with water, and the extracts are added to the alcohol-ether solution. The combined extracts are evaporated, and the residue thus obtained is dried at 100° C. for forty-five minutes and weighed. The dry, weighed residue is then dissolved in 15 c.c. of chloroform, the solution filtered through a small asbestos filter, the filter is washed with chloroform, the filtrate evaporated and the residue dried and weighed. The lipoids thus obtained are boiled with 10 c.c. of alcoholic potassium hydroxide solution, the solution is evaporated, the residue ignited at a low temperature, and the phosphoric acid estimated in the ash. In the case of dried eggs, 3 grms. of the powder are placed on a small asbestos filter and extracted with

ether; the extracted powder is then ground with 3 grms. of calcium carbonate, and the mixture is extracted with alcohol-ether, as described for flour. The extracts obtained are added to the original ether extract, which is then evaporated, and the residue of lipoids is weighed, treated with chloroform, etc. To apply the method to liquid eggs, 10 grms. of the sample are shaken with 100 c.c. of ether and 25 c.c. of 95 per cent. alcohol are added gradually; the mixture is submitted to centrifugal action, the solution decanted, and the residue heated at 75° C. for fifteen minutes with 25 c.c. of 70 per cent. alcohol. Forty-six c.c. of 95 per cent. alcohol are then added, and the mixture shaken for two minutes and for a further five minutes after the addition of 70 c.c. of dry ether. From this point the procedure is the same as that for dried eggs. Flour contains from 2·07 to 2·13 per cent. of lipoids and 0·461 to 0·531 per cent. of lipoid P_2O_5; fresh whole eggs 49·7 per cent. of lipoids and 1·299 per cent. of lipoid P_2O_5 (calculated on the dry substance).

W. P. S.

Composition of Pili Nut Oil. A. P. West and S. Balce. (*Philippine J. Sci.*, 1923, **23**, 269–276.)—A sample of pili nuts, *Canarium ovatum*, was purchased in the Manila market, the kernels removed, ground into a meal, and pressed, and after a small amount of stearin had separated from the pale yellow edible oil so obtained its constants were determined as follows:—Sp. gr., 30°/4°, 0·9069; n_D^{30}, 1·4646; iodine value (Hübl), 55·9; saponification value, 197·4; acid value, 1·42; and unsaponifiable matter, 0·19 per cent. A study of the saturated and unsaturated acids led the authors to deduce the composition of the oil to be:—Oleic glyceride, 59·6; palmitic glyceride, 38·2; stearic glyceride, 1·8; and unsaponifiable matter, 0·2; making a total of 99·8 per cent. D. G. H.

Effect of Composition on the Complete Hydrogenation of Philippine Lumbang and Pili Nut Oils. A. P. West and L. Gonzaga. (*Philippine J. Sci.*, 1923, **23**, 277–292.)—LUMBANG OIL (*Aleurites moluccana*). Hydrogenation with a 3 per cent. of nickel containing catalyst for 20 hours at practically atmospheric pressure gave a fat of melting point 67·5–71·5° C. and iodine value (Hübl) 1·08. Since the oil consists almost entirely of a mixture of linolenic (6·56), linolic (33·48), and oleic (56·98 per cent.) glycerides with 2·85 per cent. of glycerides of solid acids, the theoretical melting point should approximate 71·6° C. (as these glycerides hydrogenate to stearin), and the iodine value be reduced to 0. PILI NUT OIL (*Canarium ovatum*). The composition of this oil (see preceding abstract) is confirmed by the results of hydrogenation. After 15 hours with 3 per cent. nickel catalyst the iodine value (Hübl) was reduced to 0·96, and the melting point was 66–66·8° C. The slightly low melting point may be due to the stearin tending to dissolve in the palmitin, and the melting point of a mixture of stearin and palmitin in the same proportion in which they are found in hydrogenated pili nut oil had a melting point of 68–69° C. Hydrogenation indicates that no saturated glycerides of low melting point are present in this oil. D. G. H.

Composition of Cashew Nut Oil. A. P. West and C. C. Cruz. (*Philippine J. Sci.*, 1923, **23**, 337–344.)—The cashew nut tree (*Anacardium occidentale*) is widely distributed in the Philippines, and the fruit kernels yield an edible oil resembling olive oil, and a substance known as "cardol" is obtained from the shells. The oil used in the investigation was obtained by pressing the kernels from seeds purchased in the Manila markets, and had the following constants:—Sp. gr., 26·6°/4° C., 0·9105; n_D^{30}, 1·4665; iodine value (Hübl), 85·2; saponification value, 187·0; acid value, 1·45; and unsaponifiable matter, 1·47 per cent., with an iodine value of 94·55. The composition of the residual cake was found to be: Oil, 16·12; moisture, 2·37; ash, 3·94; protein, 31·67; crude fibre, 0·44; and carbohydrates, 45·46 per cent. An examination of the saturated and unsaturated fatty acids indicated that the oil was composed of:—Oleic glyceride, 80·4; stearic glyceride, 17·3; and unsaponifiable matter, 1·5 per cent., making a total of 99·2 per cent. D. G. H.

Anthocyans in Grapes. R. J. Anderson. (*J. Biol. Chem.*, 1923, **57**, 795–813.)—The author has isolated the pigments occurring in Norton and Concord grapes, and finds them, after purification, to be identical in composition and properties. The colouring matter consists principally of a monoglucoside, anthocyanin, which is similar to oenin derived from *Vitis vinifera*, and only differs in that it gives an intense colour reaction with ferric chloride when dissolved in alcohol. This is similar to that described by Willstätter and Zollinger for the anthocyanin obtained from *Vitis riparia*. The composition of the anthocyanin chloride corresponds to the formula $C_{23}H_{25}O_{12}Cl$. On hydrolysis with boiling hydrochloric acid it yields 1 molecule of glucose and 1 molecule of the sugar-free pigment, anthocyanidin chloride, $C_{17}H_{15}O_7Cl$. The spectrum of anthocyanin chloride consists of one broad band with indefinite margins extending from the yellow into the blue. The anthocyanidin chloride crystallises in beautiful prisms. It is very similar to oenidin chloride, which is obtained on hydrolysing oenin, but it differs in that it contains a lower percentage of methoxyl groups, *viz.* one instead of two. The anthocyanidin chloride, obtained on hydrolysing the glucoside from Concord grapes, appeared to crystallise less readily than the corresponding preparation from Norton grapes, but there was no difference in composition.
P. H. P.

Indian *Artemisia* as a Source of Santonin. (*Bull. Imp. Inst.*, 1923, **21**, 316–318.)—An examination of samples of leaves, flower buds, etc., of *Artemisia brevifolia* showed that in collections made from July 8th, to August 7th, 1922, at Garez, Kashmir, the proportion of santonin increased with the growth of the plant. The proportion of santonin in material received earlier in the year was 0·83 per cent., or 0·92 per cent. on the dry material, but the figures for the later samples were as follows, the first figure in each case representing the percentage of santonin on the wet material, and the second the figure on the dry material:—(1) Leaves and flower buds, July 8th, 0·82 and 0·92. (2) Leaves and flower buds (July 16th),

1·21 and 1·31. (3) Flower buds (July 26th), 0·97 and 1·07. (4) Flower buds (August 7th), 1·64 and 1·79 per cent. Sample (4) was found, on separation, to contain (*a*) in the flower buds and leaves (83 per cent. of sample) 1·95 per cent., and (*b*) in the stalks 1·19 per cent. of santonin. These figures show that *Artemisia brevifolia* compares favourably with *Artemisia maritima*, the usual source of santonin. D. G. H.

Microchemical Identification of Cantharidin. G. Denigès. (*Bull. Soc. Pharm., Bordeaux*, 1923–2; *Ann. Chim. anal.*, 1923, **5**, 332–333.)—About one-tenth mgrm. of the cantharidin is crushed on a micro-slide and dissolved by the addition of a drop of chloroform; the solution is allowed to evaporate, and the resulting crystals are examined without a cover slip; they are rectangular plates arranged like the steps of a ladder. If the crystals thus obtained are not well-defined, a drop of crystallisable benzene is added and allowed to evaporate. In order to confirm the result another slide is placed just over the first one, the area above the crystals is cooled by a drop of water, and the cantharidin sublimed on to the second slide by gentle heat; this produces other characteristic forms of crystals (which may be compared with those from a known cantharidin. Illustrations are given in the original. In toxicological procedure the alkaloidal solution in benzene is evaporated in the above manner, when as little as a few thousandths of a mgrm. may be detected. H. E. C.

Preparation of Commercial Glycyrrhizin. P. Bertolo. (*Giorn. Chim. Ind. Applic.*, 1923, **5**, 497–498.)—Commercial or ammoniacal glycyrrhizin consists of the normal ammonium salt of glycyrrhizic acid, usually mixed with amorphous bitter glycyrrhizin, $C_{35}H_{57}O_{13}N$, and with dark resins soluble in alcohol, yielding an alkaline solution. None of the samples examined by the author exhibited either the desired ready solubility in water to form stable solutions or freedom from appreciable bitterness. The requisite purity and solubility are attained if the liquid extract of liquorice root is concentrated to 12°Be., and the glycyrrhizic acid precipitated by treating each litre of the liquid at a temperature not exceeding 30° C., with 20 grms. of hydrochloric acid diluted with twice its volume of water. The conversion of the glycyrrhizic acid into ammonium salt is then carried out in the ordinary manner. T. H. P.

***Cannabis indica* in Smoking Tobacco. H. Henstock.** (*Pharm. J.*, 1923, **57**, 525.)—*Cannabis indica* was identified in a sample of tobacco as follows:—After drying at 50° C., weighed portions were extracted with (1) *Absolute alcohol*, which yielded a brilliant yellowish-green solution, and a residue which gave a red colour with anhydrous alcohol and hydrochloric acid solution, and when dissolved in acetic acid and treated with concentrated nitric acid, boiled, cooled and diluted with water, gave a dull orange-red precipitate which was taken to be (according to Czerkis, *Ann.*, 1907, 351, 467) the trinitro-carboxylic acid compound of cannabinol, a constituent of *Cannabis indica*. (2) *Light petroleum* which gave a

residue yielding on treatment with a few drops of concentrated nitric acid a smell of butyric acid, indicating the presence of cannabinol. (3) *Ether.* The extract, though greenish yellow in colour, was greener than that from other tobacco samples, but not so green as a pure extract of *Cannabis indica.* Further, a quantitative estimation was made by extracting a weighed quantity of the tobacco with absolute alcohol, evaporating the extract to dryness, extracting the residue with ether, and matching the colour of the solution with those of similar solutions obtained in the same way with another tobacco to which known quantities of B.P. *Cannabis indica* had been added. D. G. H.

Detection and Colorimetric Estimation of Hydrocyanic Acid. J. M. Kolthoff. (*Zeitsch. anal. Chem.*, 1923, **63**, 188–190.)—From 5 to 10 c.c. of the solution to be tested are treated with 1 c.c. of a 1 per cent. solution of sodium tetrathionate and 5 drops of 10 per cent. ammonia, and heated in a water-bath at 50° to 55° C. for 5 minutes. To the cooled solution are added 2 c.c. of 4 *N* nitric acid and 3 drops of *N* ferric chloride solution. The sensitiveness of the reaction is 0·0003 grm. of hydrogen cyanide per litre. The conversion into thiocyanate is quantitative; hence the process is suitable for the colorimetric estimation of very small quantities of cyanide: $Na_2S_4O_6 + NaCN + 2NaOH = NaCNS + Na_2S_2O_3 + Na_2SO_4 + H_2O$. The tetrathionate is prepared from equivalent quantities of iodine dissolved in alcohol, and sodium thiosulphate in strong aqueous solution; the crystals are filtered off by suction and washed with dilute alcohol. W. R. S.

Possible Discordant Factor in the Standardisation of Disinfectants. Walker and Weiss. (*The Medical Officer*, May, 1923, Reprint.)—In methods of standardisation which take phenol as the standard, such as the Rideal-Walker test, it is obviously important that the phenol should be pure. The authors point out that, when cresols are present in the phenol, bromine titration is not sufficiently delicate to detect these, and that the test employed should be based on the determination of the solidifying point, with the use of 50 c.c. of the sample. A phenol prepared synthetically solidifies at 40·5° C., whereas one containing 3·4 per cent. of cresols, whatever the particular isomer present, solidifies at 38·8° C. Cresol has three times the bactericidal efficiency of phenol; consequently it will depress the coefficient of a phenol containing it. The authors suggest that no phenol having a solidifying point below 40° C. should be used. Bromine titration should only be used as a check on the gravimetric preparation of the 5 per cent. solution. R. F. I.

Biochemical, Bacteriological, etc.

Copper as a Constituent of Milk. A. F. Hess, G. C. Supplee and B. Bellis. (*J. Biol. Chem.*, 1923, **57**, 725–729.)—The authors describe their investigations on the presence in milk of small amounts of copper by means of the ethyl xanthate method recently employed for this purpose by Supplee and Bellis (*J. Dairy Sci.*, 1922, **5**, 455). The method is based on the fact that small amounts

of copper react with potassium ethyl xanthate to produce a yellow colour, which colour is in direct ratio to the amount of copper present. A table shows the amounts of copper recovered from a sample of milk to which definite additions of a copper salt had been made and indicates that the method is reliable for as little as 0·005 mgrm. of copper in 100 c.c. of milk; investigations by the authors showed copper always to be present in larger amounts. A sample of raw cow's milk was found to contain 0·55 mgrm. of copper per litre, and samples of commercially pasteurised milk contained 0·6, 0·7 and 0·6 mgrm. respectively. From analyses, the copper content of human milk is judged to be about the same as that of the milk of the cow. These results make it appear probable that copper has some physiological action. P. H. P.

Quantitative Study of the Destruction of Vitamin *B* by Heat. H. C. Sherman and M. R. Grose. (*J. Amer. Chem. Soc.*, 1923, **45**, 2728–2738).—The authors describe the effect of 4 hours' heating upon vitamin *B* of tomato juice at 10° C. intervals over the range of 100° to 130° C. They employed the rat-growth method as a measure of vitamin *B* content. At 100° C., in acid medium, destruction occurred owing to the hot water. The following are the average figures for the destruction of vitamin *B* in tomato juice for a period of 4 hours' heating, derived by determining the size of heated doses at each temperature necessary to give weight curves approximately coinciding with those of positive controls fed with 4 c.c. of unheated juice:—At 100° C., 20 per cent., at 110° C.; 33 per cent.; at 120° C., 47 per cent.; and at 130° C., 55 per cent. A mathematical computation bringing the comparison curves into exact coincidence gives the following:—At 100° C., 24 per cent.; at 110° C., 33 per cent.; at 120° C., 45 per cent.; and at 130° C., 58 per cent. Vitamin *B*, therefore, like vitamin *C*, has a low temperature coefficient of heat destruction, only 1·3 to 1·4 at this range, as compared with 2 in most chemical reactions. The heat destruction of the vitamin, in marked contrast with the heat coagulation of typical proteins, and with the heat destruction of such typical enzymes as have been investigated, showed no increase in the temperature coefficient at temperatures in the neighbourhood of 120° C. It followed the orderly course of a chemical reaction under the accelerating influence of heat, but with a less than average temperature coefficient. P. H. P.

Investigation and Application of the Rat-growth Method for Studying Vitamin *B*. H. C. Sherman and A. Spohn. (*J. Amer. Chem. Soc.*, 1923, **45**, 2719–2728.)—The selection and care of the animals used and the basal diets given are described. Eight c.c. of fluid skimmed milk or 0·8 grm. of dry milk per rat per day, when fed separately on the basal ration, were the quantities chosen as being most advantageous to give in order to detect possible reduction in vitamin *B* content on heating. It is believed to be possible to detect a diminution, certainly of 25 per cent., and probably of 15 per cent., in the vitamin *B* content of the food tested when dealing with averages of 10 or more suitably chosen rats on each diet. Vitamin *B* in the form in which it exists in milk is comparatively stable to heating

at 100° C. in the dry state, no diminution being noticed after 48 hours of heating with free access of air, but it is less stable when heated at 100° C. in aqueous solution. After 6 hours there was an apparent diminution; probably a fourth of the vitamin was thus destroyed. P. H. P.

Two Methods for Studying Vitamin *B*. H. C. Sherman and H. Edgeworth. (*J. Amer. Chem. Soc.*, 1923, **45**, 2712–2718.)—The authors have examined the availability of the gravimetric yeast-growth method and of the rat-growth method for the quantitative study of vitamin *B* and their experiments are described. Both methods yield quantitative results. The probable errors of the averages obtained in the different series by the former method are of the order of 1 per cent., and by the latter method of 2 to 4 per cent., of their numerical values. The increased growth of yeast may, however, be due to the introduction of other substances favourable to yeast growth. The rat-growth method is therefore considered preferable, in spite of the larger probable errors, since the results can be interpreted in terms of vitamin *B* with much greater certainty. P. H. P.

Toxicological and Forensic.

Solubility of Mercuric Sulphide in Ammonia and its Influence on the Detection of Arsenic in the Presence of Mercury. C. Ghigliotto. (*Ann. Chim. anal.*, 1923, **5**, 326.)—The precipitate which always forms on passing hydrogen sulphide through the solution obtained in the destruction of organic matter by the wet method commonly used in toxicological analysis invariably contains organic matter, as well as mercury sulphide, if any. If this precipitate is treated, as usual, with ammonia the mercury is partially dissolved, and this may give rise to two errors; the presence of mercury may be overlooked if the precipitate entirely dissolves, or the presence of mercury in the filtrate may prevent the formation of the mirror due to arsenic when the solution is treated by the Marsh process. H. E. C.

Composition and Toxicity of the Arsenobenzenes. Estimation of Arsenic in these Products. M. de Myttenaere. (*Bull. de l'Acad. Roy. Med. Belg.*, 1923, **3**, 258; *J. Pharm. Chim.*, 1923, **28**, 357–362.)—The method of estimating the arsenic is based upon its oxidation by means of 10 vol. hydrogen peroxide. The sample (0·2 grm.) is placed in a 200 c.c. conical flask and dissolved in 5 c.c. of water. Ten c.c. of hydrogen peroxide are added, followed by 10 c.c. of 50 per cent. (by weight) sulphuric acid, and the mixture gently boiled on a sand bath. When decomposition of the hydrogen peroxide is complete, the liquid is cooled, a further 5 c.c. of sulphuric acid added, and the whole re-heated until colourless and white fumes of sulphuric acid are formed. Ten c.c. of water are then carefully added, and a few drops of 1 per cent. potassium permanganate solution till the colour persists. Decolorisation is then effected by means of 2 per cent. oxalic acid, 20 c.c. of 25 per cent. potassium iodide solution are added, and the liquid heated for 20 minutes on a water bath, cooled, and exactly decolorised with

0·1 *N* sodium thiosulphate. Twenty-five c.c. of a cold saturated solution of sodium carbonate are next added, and an excess of sodium bicarbonate, and the arsenic in the original 0·2 grm. estimated by titrating the solution with 0·1 *N* iodine solution, and multiplying the number of c.c. required by 0·003748.

In considering the formula of the arsenobenzenes one notes that there are 2 arsenic and 2 nitrogen groups in the central nucleus, whatever the composition and complexity of the side chains— $\left(\frac{As}{N} = \frac{75}{14} = 5{\cdot}357\right)$. Thus a product containing arsenic and nitrogen in the theoretical proportions should give figures for arsenic and nitrogen as 5·357 is to 1. Toxic products are shown to have a deficiency of nitrogen in proportion to arsenic. Further, in such toxic products the amount of arsenic precipitated by hydrogen sulphide (DM1) increases in proportion to the toxicity; it is estimated as follows:—One grm. of the product is dissolved in 90 c.c. of boiling distilled water, 10 c.c. of 30 per cent. acetic acid added, and the whole heated in a steam bath (with stirring from time to time) for 10 minutes from the time precipitation begins. After cooling and filtering, the clear filtrate is heated to about 60° C., 5 c.c. of hydrochloric acid added, and hydrogen sulphide passed in to saturation. After standing and filtration, the precipitate is washed with warm water, digested with 20 c.c. of ammonium carbonate solution, washed with distilled water, and the ammonium carbonate boiled off on a water bath. Ten c.c. of hydrogen peroxide and 10 c.c. of 50 per cent. sulphuric acid are carefully added, and the liquid evaporated till white fumes appear. A few drops of 1 per cent. potassium permanganate solution are added, and the operation continued as above. The number of c.c. used in the titration (DM1) should not exceed an outside limit of 12, but in the course of the investigation some ampoules of the same series were found to give varying results, probably owing to faulty vacuum and oxidation, and details of a study of this point are given. Particulars are also given for the estimation of the additional amount of arsenic found in the various precipitates encountered in the investigation, and the composition of these precipitates is discussed. The general conclusion drawn is that a product which may be regarded as satisfactory from the toxicological point of view should contain a total amount of arsenic between 19 and 21 per cent., that the ratio of arsenic to nitrogen should not exceed 5–6, and that (DM1) must not exceed 12. D. G. H.

Toxicological Detection of Minute Quantities of Nitric Acid. C. Ghigliotto. (*Ann. Chim. anal.*, 1923, **5**, 325.)—The membranes and muscles of the stomach act as a mordant in combining with nitric acid, even in very dilute solutions, as does the skin when it forms the familiar yellow stain with the strong acid. This forms the basis of the following method for the detection of the acid in the stomach in quantities far too small to be detected by the ordinary process of distillation. Pieces of the membrane are washed with water, dried between filter paper, and a few drops of diphenylamine in sulphuric acid are added; the characteristic blue colour is developed, even with the acid so dilute as 1:1000.

H. E. C.

Water Analysis.

Estimation of Dissolved Oxygen in the Presence of Iron Salts. A. M. Buswell and W. U. Gallager. (*J. Ind. Eng. Chem.*, 1923, **15**, 1186–1188.)—The Rideal and Stewart modification of the Winkler method for the estimation of dissolved oxygen in waters yields high results when the water contains iron salts; the presence of 1 part per million of iron causes the result for the oxygen to be from 0·1 to 0·13 part per million too high, but a satisfactory correction cannot be applied, since, according to circumstances, from 75 to 90 per cent. of the iron reacts. Trustworthy results may, however, be obtained by Mohr's method as modified by Levy, in which ferrous iron in alkaline solution is oxidised by the dissolved oxygen. A portion of the water is treated with standard ferrous iron solution, then rendered alkaline with potassium hydroxide solution and acidified; another similar portion of the water is acidified, and then treated with the ferrous iron solution. Both portions are titrated with permanganate solution and the difference between the two titrations is proportional to the amount of dissolved oxygen present. The apparatus used consists of a bulb with a tap at each end and a funnel at one end for the introduction of the reagents. W. P. S.

Agricultural Analysis.

Estimation of the Sulphur Compounds in Dry Lime Sulphur. C. P. Jones. (*J. Agric. Res.*, 1923, **25**, 323–336.)—When carbon dioxide is passed through a solution of polysulphide the monosulphide sulphur is completely separated from the thiosulphate and residual sulphur; this fact forms the basis of the following method for the estimation of the three forms of sulphur in dry lime-sulphur. About 0·5 grm. of the sample is placed in a dry flask fitted with inlet and outlet tubes and a dropping funnel. The inlet tube delivers a stream of carbon dioxide which has been passed through sodium bicarbonate solution (to remove traces of free acid) and through sulphuric acid. The outlet tubes pass into two wash bottles which contain 100 c.c. of hydrated sodium peroxide solution. After all air has been displaced by the carbon dioxide 50 c.c. of water are run into the flask, which is then shaken for five minutes without interrupting the current of gas, and the gas passed until all the hydrogen sulphide has been expelled and absorbed by the alkaline solution. The contents of the flask are filtered through asbestos, and the filtrate diluted and titrated with 0·05 *N* iodine solution to estimate the thiosulphate. The sulphur on the filter and any adhering to the tubing is washed with dilute hydrochloric acid, dried at 100° C., weighed, ignited, and again weighed; the difference gives polysulphide sulphur together with any free sulphur. The sulphur evolved as hydrogen sulphide is oxidised to sulphate by the peroxide solution, which is then boiled and the sulphate precipitated with barium chloride. H. E. C.

Estimation of Nitrate Nitrogen in the Presence of Cyanamide and some of its Derivatives. K. D. Jacob. (*J. Ind. Eng. Chem.*, 1923, **15**, 1175–1177.)—An aliquot portion of the solution containing nitrate, urea, cyanamide, dicyanodiamide, etc., is neutralised and treated with 10 c.c. of a neutral 2 per cent. extract of jack-bean flour; after one hour the urea present will have been converted into ammonia and carbon dioxide. The mixture is then treated with 100 c.c. of saturated silver sulphate solution and 10 c.c. of 15 per cent. potassium hydroxide solution, and filtered after one hour, and the precipitate is washed six times with 10 c.c. portions of water. This treatment removes the cyanamide, dicyanodiamide and guanyl-urea. The filtrate is diluted to 350 c.c., treated with 5 c.c. of 20 per cent. sodium hydroxide solution and distilled to remove ammonia; 300 c.c. of distillate are collected. Two hundred c.c. of water and 2 grms. of Devada's alloy are then added to the residual solution in the distillation flask, and the distillation is continued, 200 c.c. of distillate being collected in a definite volume of 0·1 *N* sulphuric acid contained in the receiver. The excess of acid is titrated subsequently, and the ammonia thus found represents the nitrate present in the original solution. W. P. S.

Organic Analysis.

Estimation of Phosphorus in Organic Substances. J. Garola. (*Ann. Chim. anal.*, 1923, **5**, 326–328.)—The ordinary incineration of organic matter leads to the loss of phosphorus, and the destruction of large quantities of such material by the Kjeldahl process is tedious. Accurate results may be obtained by ignition in the presence of calcined magnesia. To about 5 grms. of the mixture to be examined is added about 0·2 grm. of magnesia, which is intimately mixed in by making a paste of the mixture with water and drying on the water bath prior to the ignition. The ash is extracted with dilute hydrochloric acid, the solution filtered and diluted to about 100 c.c., and the phosphate precipitated as ammonium phosphomolybdate. H. E. C.

Detection of Esters of Fixed Acids in Essential Oils. A New Method of Testing. C. T. Bennett and D. C. Garratt. (*Perfumery and Ess. Oil Record.*, 1923, **14**, 359.)—As little as one per cent. of ethyl citrate, tartrate, succinate, benzoate, phthalate or cinnamate may be detected in essential oils by the following simple procedure:—One c.c. of the essential oil and 3 c.c. of an approximately 10 per cent. solution of potassium hydroxide in absolute alcohol are placed in a test tube, and the whole heated in a water bath for a few minutes and cooled. The oil may be regarded as unadulterated with the above esters if no precipitate is formed in, at most, an hour. Ethyl phthalate (2·5 and 1·0 per cent.) very quickly causes a precipitate; with 2·5 per cent. of the cinnamate a precipitate forms rapidly, and with 1 per cent. more slowly; with 2·5 per cent. of the succinate a gelatinous mass results, and with 1 per cent. a crystalline precipitate; citrate and

tartrate cause cloudiness and crystals are precipitated on standing; with 2·5 per cent. of benzoate precipitation is slow. The test appears to be specially delicate for phthalic esters. D. G. H.

Estimation of Pentoses and Pentosans. 1. The Formation and Distillation of Furfuraldehyde. N. C. Pervier and R. A. Gortner. (*J. Ind. Eng. Chem.*, 1923, **15**, 1167–1169.)—The usual method of estimating pentoses consists in distilling the substances with 200 c.c. of 12 per cent. hydrochloric acid at such a rate that 30 c.c. of distillate are collected in ten minutes; 30 c.c. more of the 12 per cent. acid are then added to the distillation flask and the process is repeated until 360 c.c. of distillate have been collected. The resulting furfuraldehyde is estimated in the distillate. It is shown that during this process of distillation the concentration of the acid varies from 12½ to 20 per cent. and that the stronger acid has a destructive effect on the furfuraldehyde, thus causing the method to yield low results. The following method of distillation prevents loss of the aldehyde:—A quantity of 0·2 to 5·0 grms. of the substance (according to the pentose or pentosan content) is placed in a distillation flask, together with 200 c.c. of 12 per cent. hydrochloric acid (sp. gr. 1·06), and a slow current of steam is led into the mixture; as soon as the liquid boils the flask is heated by means of a small burner so that the temperature of the vapours is maintained between 103° and 105° C., as measured by a thermometer in the neck of the flask. The steam distillation is continued until a drop of the distillate no longer gives a red coloration after three minutes' contact with a drop of aniline acetate solution on a filter paper. Theoretical yields of furfuraldehyde were obtained when this method was applied to *l*-arabinose and *d*-xylose. W. P. S.

Quantitative Variation of Gossypol and its relation to the Oil Content of Cottonseed. E. W. Schwartze and C. L. Alsberg. (*J. Agric. Res.*, 1923, **25**, 285–295.)—Examination of many varieties of cottonseed has proved the presence of gossypol in the kernels of all varieties and the husks of some. The amount is very variable, being from 0·4 to 1·2 per cent. even in different samples of the same variety on the same plantation in different years, but is proportional to the oil content. Estimation of the gossypol is carried out by a modification of Carruth's aniline method (ANALYST, 1918, **43**, 222.) Seventy-five grms. of the sample are thoroughly extracted in a Soxhlet tube with ether, which is then distilled off and the extract dissolved in 8 volumes of petroleum spirit. After standing overnight the flocculent precipitate, which usually appears, is filtered off and washed with ether, the washings evaporated, and the residue dissolved in petroleum spirit and added to the main solution. One c.c. of aniline is added, and the mixture shaken for 5 minutes, or until all the aniline is dissolved, then set aside for 3 to 7 days, after which the aniline-gossypol is filtered on to a Gooch crucible, washed with petroleum spirit, dried at 100° C. and weighed. The weight of the precipitate, less the weight of the aniline in it (N × 6·64), gives the weight of the gossypol. The latter may be identified by means of its acetate, the crystallographic details of which are given in the paper. H. E. C.

Chrome-leather Analysis. International Commission Report. R. F. Innes. (*J. Soc. Leather Trades Chem.*, 1923, 413.)—An official method for estimating chromium has been adopted in the leather trade. It consists in fusing in a nickel crucible the ash from 5 grms. of the sample with five times its weight of sodium peroxide for one to five minutes at a moderate red heat. The fused mass is allowed to cool, dissolved in hot water, and boiled for 10 minutes in the presence of a clean piece of thin sheet iron, about half-an-inch square. The solution is filtered, the residue washed, and filtrate and washings diluted to 500 c.c. One hundred c.c. are then acidified with hydrochloric acid free from chlorine, and the chromium estimated iodimetrically.

An alternative and quicker method is also allowed:—The ash from 5 grms. of the sample is mixed and ignited in a platinum crucible with three to four times its weight of a mixture of equal amounts of magnesia and sodium carbonate for one minute. The mixture is carefully and thoroughly ground in an agate mortar till homogeneous and roasted again in the platinum crucible at a bright red heat for ten minutes. The mixture is then dissolved in excess of dilute hydrochloric acid, and the chromium estimated iodimetrically.

A provisional method has been adopted for estimating free sulphur and grease by extracting the sample in a Soxhlet extractor for 3 hours with petroleum spirit. The free sulphur alone is estimated by treating the mixture with fuming nitric acid at laboratory temperature for 3 days, whereby sulphuric acid is formed; this is subsequently estimated gravimetrically. R. F. I.

Effect of Perspiration on Chrome Upper Leather. R. F. Innes. (*J. Soc. Leather Trades Chem.*, 1923, 436.)—A glacé kid shoe-front had worn very badly and become very firm, badly cracked and dull in appearance. This effect had been produced by wear on a hot foot. A strip about $\frac{1}{4}$ inch wide outside the stitches was cut off, as this showed the bright glaze and had apparently been protected from the action of the perspiration. The two pieces were analysed, and showed the following results:

	Cracked.	Unaffected.
Chromic oxide, per cent.	1·71	1·90
Sodium chloride, per cent.	2·75	0·69
Behaviour on boiling	much shrivelled	somewhat shrivelled

The low chromium indicates a semi-chrome leather. Perspiration evidently has a deleterious effect on this type of leather. R. F. I.

Inorganic Analysis.

Colorimetric Estimation of Small Quantities of Bismuth. L. Cuny and G. Poirot. (*J. Pharm. Chim.*, 1923, **28**, 215–223.)—The method is based upon the fact that if an aqueous solution of quinine sulphate and potassium iodide is added to a solution of a bismuth salt containing sufficient gum arabic, no precipitate of iodobismuthate of quinine is formed, but a yellow colour develops similar to that of potassium dichromate solutions.

After experimenting with different strengths of reagents and conditions of reaction, the following method of procedure was adopted: Solutions required are (1) *Stock solution of bismuth.* Dissolve 2·23 grms. of bismuth oxide in 10 per cent. nitric acid and make up to a litre. (2) *Standard solution of bismuth.* Take 25 c.c. of solution (1), add 175 c.c. of 10 per cent. nitric acid, and make up to a litre with distilled water. Five c.c. of this solution will thus contain 0·25 mgrm. of bismuth and 0·1 mgrm. of nitric acid. (3) *Quinine nitrate.* Dissolve 1 grm. of the hydrate in 5 c.c. of 10 per cent. nitric acid, and make up to 100 c.c. with distilled water. (4) *Five per cent. potassium iodide solution.* (5) *Ten per cent. gum arabic solution in ampoules.* Five c.c. of the standard solution and 5 c.c. of the solution to be examined are respectively measured into dry test tubes, 3 c.c. of the gum arabic and 1 c.c. of the potassium iodide solution added, with shaking after each addition, and the colours compared in a Dubosq colorimeter. The standard solution is at a height of 5 mm., and the height found on matching the second solution should lie between 4 and 7 mm., suitable dilution of one or other of the solutions being effected if necessary. Under these conditions the proportion of bismuth is found from the formula—$x = \frac{50 \times 5}{n}$, where n is the reading obtained. Where bismuth was estimated by this method in solutions of known strength the percentage error in 6 estimations varied from $-0{\cdot}3$ to $+3{\cdot}5$. Errors are introduced by the presence of free hydrochloric, sulphuric and acetic acids, traces of nitrogenous substances capable of decomposing the potassium iodide, and salts of metals, although in the last case the gum arabic tends to prevent the formation of precipitates and to give colloidal solutions. D. G. H.

The Gravimetric Ratio—Antimony : Antimony Tetroxide. J. Knop. (*Zeitsch. anal. Chem.*, 1923, **63**, 181–188.)—Finely powdered antimony of known purity was carefully oxidised with nitric acid and the dry oxide heated for one hour at 850° to 900° C. in an electric furnace, the temperature of which was observed by means of a thermo-couple. The experiments, which were carried out with every precaution to ensure an accuracy of $\pm 0{\cdot}0001$ grm., gave the equivalent Sb = 122·04, or 121·94 after reduction to weight *in vacuo*. The tetroxide obtained was distilled with hydrochloric acid and potassium iodide in an atmosphere of carbon dioxide, and the iodine titrated with thiosulphate solution standardised against dichromate; these determinations gave a mean of 121·98. W. R. S.

Separation of Radium and Barium. V. Chlopine. (*Bull. Soc. Chim.*, 1923, **33**, 1547–1551.)—The method of separating radium and barium elaborated by the author is based on the regular diminution produced in the solubility of barium chloride in water by gradual addition of hydrochloric acid, and on the fact that, when gaseous hydrogen chloride is passed into a solution of barium chloride containing radium, the precipitated chloride is richer in radium than the chloride remaining dissolved. This method is as effectual as fractional crystallisation with the help of evaporation; it also allows of the ready variation of the

coefficient of enrichment within wide limits and does not require preliminary purification of the chlorides; the presence of lead is without harmful effect on the coefficient of enrichment. T. H. P.

Identification of Amines. C. S. Marvel and F. E. Smith. (*J. Amer. Chem. Soc.*, 1923, **45**, 2696–2698.)—In the Hinsberg test (*Ber.*, 1890, **23**, 2963), *p*-bromobenzenesulphonyl chloride cannot be used in place of benzenesulphonyl chloride, because, although it gives easily crystallisable *p*-bromobenzenesulphonyl amides with sharp melting points (these being especially good for ethyl aniline, *n*-propylaniline, *n*-butylaniline and piperidine), yet, with many primary amines it gives alkali-insoluble derivatives. The preparation of *p*-bromobenzenesulphonyl chloride is described. The amide is prepared by treating the chloride with a slight excess of the amine and warming, if necessary, to start the reaction, which takes place smoothly with the evolution of heat and is complete in a few minutes. The product is washed with dilute hydrochloric acid, to remove excess of amine, and then recrystallised from alcohol. Methylamine, dimethylamine and piperidine derivatives are prepared by the action of *p*-bromobenzenesulphonyl chloride and aqueous alkali in the usual manner on an aqueous solution of the amine hydrochloride. The following is a list of certain amines with the melting points of the corresponding para-bromobenzenesulphonamides:—Methylamine, 77° C.; benzylamine, 117° C.; dimethylamine, 94° C.; piperidine, 91° C.; *o*-toluidine, 116° C.; *p*-toluidine, 98° C.; *p*-anisidine, 142° C.; *p*-phenetidine, 143° C.; *α*-naphthylamine, 183·5° C.; and *β*-naphthylamine, 129° C. P. H. P.

Hypobromous Acid and Estimation of Hypobromous and Bromic Acids. E. Biilmann and E. Rimbert. (*Bull. Soc. Chim.*, 1923, **33**, 1465–1473.)—For estimating bromic and hypobromous acids together use may be made of the fact that the latter acid reacts instantaneously with excess of phenol, forming brominated derivatives which have no action on potassium iodide, whereas bromic acid does not react with phenol, but liberates iodine from the iodide in presence of dilute sulphuric acid, and may thus be estimated by subsequent titration of the solution with thiosulphate. In concentrated solutions the reaction between bromic and hydriodic acid takes place sufficiently rapidly, but the liquid should then be diluted before titration with thiosulphate; when dilute solutions are used, the reaction should be accelerated by means of a catalyst, such as ammonium molybdate (ANALYST, 1921, **48**, 160). Trial analyses on these lines yielded satisfactory results. T. H. P.

Physical Methods, Apparatus, etc

Method for the Separation of Gas Mixtures. M. Shepherd and F. Porter. (*J. Ind. Eng. Chem.*, 1923, **15**, 1143–1146.)—A method is described for the separation of the constituents of a gas mixture by fractional distillation at low temperatures and pressures. The apparatus used consists of one complete unit combining all the parts necessary for condensation, distillation, pumping, storage, measurement, and distribution. The distillation bulbs are surrounded

by Dewar tubes containing liquid air, and these tubes are connected with a vacuum pump or mercury pressure seals, so that the air may be made to boil at pressures varying from 0·1 to 2 atmospheres and at a corresponding temperature of −180° to −208° C. Details of the application of the method to the analysis of a gas mixture containing helium, nitrogen, methane, ethane, propane, butane and higher saturated hydrocarbons are given. W. P. S.

Behaviour of Pumice Stone during the Dehydration of Organic Liquids. A. Seidenberg. (*J. Assoc. Off. Agr. Chem.*, 1923, **7**, 99–106.)—Ignited pumice stone readily absorbs moisture from liquids spread over it, and this absorbed moisture can only be removed completely by again heating the pumice to redness. The absorbed moisture has also a decided effect in accelerating the decomposition of organic substances spread over the surface of the pumice, which is, therefore, an unsuitable substance to use in aiding the drying of these liquids. If the temperature used is low, all the moisture is not expelled, and at a higher temperature it is not possible to distinguish between loss due to decomposition and loss due to evaporation of water. W. P. S.

Colour Measurement of Tanning Materials. T. Blackadder. (*J. Soc. Leather Trades Chem.*, 1923, 445.)—This method obviates the faults in the Lovibond method due to partial colour-blindness in different observers, those due to varying illumination, and those due to the optically impure standard glasses. (It is possible to match a chestnut extract with or without blue in the combination at will). Theoretically one can measure coloured light qualitatively by resolving it by means of a spectroscope which shows the absence or preponderance of certain colours or wave-lengths. To measure these quantitatively one should measure the amount of every wave-length, but a practical approximation can be obtained by measuring a large number of the wave-lengths at scattered parts of the spectrum. If one passes a beam of light through a tannin solution one can measure the intensity of as many wave-lengths as is considered practicable and express this in terms of the intensity of the original beam, thus obtaining a specific measure of the colour of the light passed by the solution and also of the amount absorbed by the solution. In this way one is independent of the purity of the original source of light. Trials have shown that four particular regions are most suitable for tannin solutions:—Red, passing wave-lengths of 700–600; yellow, passing wave-lengths of 550–600; green, passing wave-lengths of 510–550; and blue, passing wave-lengths of 400–510. For other solutions, such as dyes or oils, another set of three or four regions might be more suitable.

In practice, use is made of a double field of some design which is evenly illuminated when distilled water is in the position afterwards occupied by the solution. The incident light passes through a variable opening in a rotating sector to the first half of the field and through a cell containing the tannin solution to the second half. A half light is used on the first half by the use of a neutral tint filter of 50 per cent. transmission or a rotating disc, one half of which has been cut away. The thickness of the test solution is varied till a match to this is

obtained. Therefore the lighter the colour of the solution, the greater the proportion of the light it will pass and the higher the measurement. This is the reverse of the Lovibond method.

The apparatus used is of the type described by Schmidt and Haensch (*J. Amer. Leather Chem. Assoc.*, **1922**, 209). The individual measurements are made by observing the field of the instrument through each of the four colour filters in turn. These with the neutral tint filter can be obtained from the Eastman Kodak Company already standardised. The concentration of the tannin solution is 0·4 per cent., as used in the official analytical method. Readings are given of several tannin extracts by the new method; also a comparison of it with the Lovibond method. Another method of expressing the results is to reduce the red readings to 10·0 and the other colours in proportion. R. F. I.

Note by Abstractor.—Attention may be drawn to Prof. Procter's paper on this subject in *J. Soc. Chem. Ind.*, **42**, 73T–79T; ANALYST, 1923, **48**, 405.

Method of Micro-incineration applicable to Histo-chemical Investigations. A. Policard. (*Bull. Soc. Chim.*, 1923, **33**, 1551–1558.)—Before being sectioned, the tissue or organ is fixed by means of a coagulating agent which neither adds nor removes mineral constituents. Neither acid nor saline fixing agents, such as bichromates, mercuric chloride, etc., should be used. The most satisfactory agents are alcohol and formaldehyde, although the former cannot be used when phosphorus is sought, since it removes phosphorus-containing lipoids. The fixed material is frozen by means of solid carbon dioxide and cut into sections, which are collected in water or alcohol and then spread on slides and dried, away from dust, at first in the air and later in an oven at 58° C.; a final drying at 105° C., prior to incineration, is also advisable. The incineration is best effected by raising the temperature in 12 to 15 minutes to dull redness. For this purpose use may be made of a small electric furnace consisting of a quartz tube surrounded by a resistance and by a suitable asbestos covering. The glass slide is conveniently supported either on unglazed porcelain or on platinum foil and this on asbestos card; inclination of the tube causes a slight draught, which favours the calcination.

The ash is viewed by reflected light under a magnification of 60 or, better, 150 diameters, which renders possible the distinction of many elements, especially of those of the cellular nucleus. A lamp similar to the Stiassnie ultra-microscopy lamp permits a convenient orientation of the light. The fragile ash may be protected by a cover-glass fixed at the corners with paraffin-wax. T. H. P.

Reviews.

LABORATORY MANUAL OF PHYSICAL CHEMISTRY. A. W. DAVIDSON and H. S. VAN KLOOSTER. Pp. 182. New York: John Wiley & Sons; London: Chapman & Hall. 1922. Price 10s. net.

This volume will certainly be useful for the somewhat narrow purpose for which it is intended. It is designed to assist the instructor in handling a large class of beginners, and to enable the students to record the results of a large number of experiments in a minimum of time. This narrow scope obviously restricts the general utility of the book, but, bearing in mind the avowed object, it must be said that the volume presents good points—and some bad ones.

There are described in detail the method of carrying out some twenty-four well-selected experiments covering the range of physical chemistry usually required from university students not reading for honours in this branch. With the possible exception of the Emerson type of bomb calorimeter, all the apparatus described is that common to well-equipped laboratories. For each of the experiments there is given a list of references to theoretical text-books dealing with it, a list of apparatus required, an illustration and blank spaces for recording the results of observations; the book therefore is to serve as a note-book as well as a text-book. The production of the book is excellent in printing, paper and cost. Very few errors were observed, as is to be expected from such experienced authors.

There is a decidedly American style about the volume; although containing an abundance of blank pages and waste space the abbreviations frequently used are a blemish, "vis. and surf. tens." for "viscosity and surface tension" may be allowable in a laboratory note-book, but such expressions do not look well in print. Most chemists, even elementary students, do not need telling for each experiment that a Bunsen burner requires rubber tubing, or that a condenser requires the support of an iron stand; if such a hint is necessary, the many excellent drawings suffice to give it. Had much of the repetition in the lists of books and apparatus been withheld there would have been space for the methods of calculation and a brief statement of the theory underlying the experiments. It appears that the student goes the round fitting up apparatus laid out like "Meccano" parts and reading results. This method seems to detract from the educational value of the work, but doubtless assists in the turning out of chemists, like Ford cars, by the million.

H. E. COX.

SECOND YEAR COLLEGE CHEMISTRY. WILLIAM H. CHAPLIN. Pp. xi.+311. New York: John Wiley & Sons; London: Chapman & Hall. Price 15s. net.

A review of the laboratory companion of this text-book appeared in THE ANALYST for last June, and many of the comments made there apply also to this volume. The title is a misnomer; "Outlines of Physical Chemistry" would convey a more accurate impression of the scope of the work.

In addition to the subjects referred to in the above-mentioned review, this book contains chapters on the Periodic system, Radioactivity and Atomic Structure; the two latter give an up-to-date account of radioactive transformations, and introduce recent work of Rutherford, Langmuir and others on the constitution of atoms. Many of the chapters commence with a useful outline of the historical development of the subject, and the treatment throughout is clear and concise; the illustrations are easy to follow and sufficiently numerous for their purpose; a considerable variety of test questions is also provided.

A particularly satisfactory section is that on indicators, the discussion of this subject being unusually complete, although the P_H notation might, perhaps, have been introduced with advantage. On the whole, this volume leaves a more favourable impression than its laboratory companion, and it can be recommended for the study of elementary physical chemistry. A reduction in price would put this book more on a level with others on the same subject. A. F. KITCHING.

REDWOOD AND EASTLAKE'S PETROLEUM TECHNOLOGIST'S POCKET BOOK. 2nd Edition. Pp. 546. London: Charles Griffin & Co., Ltd. 1923. Price 15s. net.

One can only say of this book that it appears to be a compendium of all the information that a prospector for oil could possibly require—general, statistical, geological, legal, or linguistic. Surface indications, testing for oil, trial borings, purchase or leasing of land (in any country, speaking any language), storage, transport, refining of the product, all are described. To indicate the variety of its contents even in summary would require several times the space that could be allotted to a review in the ANALYST, and those really wishing to know what is in the book must consult the table of contents, itself occupying 16 pages, or the excellent index.

Much of the matter, such as the capacity of wheelbarrows, the force of the wind, the sizes of wire nails, the Roumanian for seventeen, or the distance from Constantinople to Dover, is only of secondary interest to analytical chemists; but the book is a mine of such miscellaneous information, all, of course, bearing on one phase or other of the petroleum industry.

The most useful portions of the book to chemists are the long tables of specific gravities and of the results of fractional distillation of actual individual samples of oils from every part of the world, of the composition of natural gases, asphalt rocks and refined asphalts; and the similar, though smaller, collection of calorific values and specific heats of oils. Matter is brought together here which, without this book, it would be very difficult and tedious to find.

The testing of petroleum and of asphalts is mentioned: but for the most part individual tests are merely enumerated, or the methods of carrying them out indicated in the most general terms. Whilst this is all that is done for such common constants as specific gravity, viscosity, or flash point, or for the fractionation of oils by distillation, yet the method for the quantitative bromination

of an oil is quoted at length and in detail from Allen's *Organic Analysis*. It seems to the reviewer that either this process should have been merely indicated, like the others, or that some space should have been devoted to a description of the methods used in determining the various constants mentioned.

There are, of course, the usual tables of weights and measures of all nations, and tables for their conversion into metric equivalents, and the conversion of hydrometer readings and thermometric scales, which make one once more marvel at the perversity of mankind in refusing to rid themselves of the useless and wasteful labour which the existence of such tables implies; and there are some unusual and useful (the pity is that such things should be useful) tables for the mutual conversion of the readings of Redwood, Engler, and Saybolt viscometers. The figures, as far as the reviewer has tested them, seem to have been carefully edited, and errors are rare, though there is rather a bad one in the formula given on page 308 for the capacity in imperial gallons of a barrel or cask. One regrets the misuse of language involved in the use of the term "water white" for colourless; but its use by either a poet or a petroleum prospector does not merit the same reprehension as its issue in a specification for "Benzole" by a professedly scientific body like the Engineering Standards Association. Yet who knows what effect the term may have on the morals of a man who is thinking of adulterating milk? The style of the book is excellent, all the work in it seems to be very well done, and the index makes it all readily accessible. To the petroleum technologist the book must be invaluable, and the chemist will find in it much valuable material that he will not easily find elsewhere. J. T. DUNN.

THE MANUFACTURE OF NITRIC ACID AND NITRATES. By A. COTTRELL, M.Sc., F.I.C. (Lunge and Cumming). Pp. xv. + 454. London: Gurney & Jackson. 1923. Price 36s. net.

This is the third volume to appear of the revised edition of Lunge, which is being edited by Dr. Cumming. This volume deals somewhat exhaustively with nitric acid manufacture, and the making and handling of mixed sulphuric and nitric acids for nitration purposes, and will prove of especial interest to those connected with the manufacture of explosives.

Chapter I. deals with the production of nitrate of soda from the natural deposits in Chili, and with the various main processes of extraction and separation. Chapter II. deals with the manufacture of nitric acid by distillation of Chili saltpetre with sulphuric acid, and includes detailed particulars furnished by several large works of general working methods; this chapter also discusses the concentration and recovery of weak nitric acid, and the costs of working, and a valuable section is contributed by Dr. G. A. Welsh, the Medical Superintendent at the Gretna Factory, on acid burns, poisoning, and general medical equipment. Chapter III. deals with methods of analysis, and nitre-cake; Chapter IV. with denitration of waste acids; Chapter V. with the mixing of acids for nitration purposes and the methods of doping and production of mixed acids of requisite

strengths; Chapter VI. deals with chemical and physical properties of nitric acid; Chapter VII. with those of industrial nitrates and production of same; while Chapter VIII. reverts to mixed acids and the calculation of mixes for nitration purposes.

The book is well written, and the grouping of references, patents and analyses together at the end of each section will be found useful when any particular point is being looked up. The emphasising and frequent repetition of somewhat obvious details will be valuable to a novice, but are rather too prominent in a work of this class, which, on the whole, should be a valuable reference book for the technical man. The sections dealing with the mixing and doping of acid mixes, and the mathematical factors involved are very fully written, are set out clearly, and should prove very useful to those who have to deal with acid mixing; also the acid balance at the end of the book is a valuable example of how the rather complicated requirements of an explosives factory in regard to acids can be worked out and covered.

It would have been an advantage if all the methods of analysis had been grouped together in one chapter, as this would have avoided repetition and cross references. Also, formulæ should be given, to make tests which are not obvious, perfectly clear, as on p. 31. (Test for Iodates), and on p. 244, (Test for Nitrous Acid).

There are very few misprints, but on p. 155 the author gives 80 per cent. nitric acid as being commonly produced from Glover tower acid and ordinary nitrate; this should be 80° Tw. or 65 per cent. In Chapter VII. the author deals with the manufacture of ammonium nitrate, and refers to the U.S.A. plant at Perryville; it would have been useful if more details could have been given of the very large plants erected for this purpose in this country, especially of the Swindon factory, as, doubtless, the industrial application of the phase rule to mixed solutions will be of increasing importance in years to come.

The collection of patents and extracts therefrom in reference to the subjects treated take up a considerable portion of the book, and in future editions might, with advantage, be further curtailed; in fact, the whole book could be further condensed without seriously detracting from its utility.

The author has compiled a very full and extensive text-book which is a valuable record of experience gained on large scale plant for the manufacture of nitric acid. It will be valuable to both the student and the technical man, and should be included in every technical chemical library. H. J. BAILEY.

Publications Received.

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Vol. I. 5th Edition. J. & A. Churchill. 1924. Price 30s. net.

CANNED FOODS IN RELATION TO HEALTH. By W. G. SAVAGE, M.D. Cambridge University Press. Price 8s. 6d. net.

THE CHEMISTRY AND PHYSICS OF CLAYS. By A. B. SEARLE. Ernest Benn Ltd. Price 55s. net.