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An Attempt to Extend Mitchell's Colorimetric Method to the Estimation of Catechol Tannins.

(Work carried out under the Analytical Investigation Scheme.)

BY PHYLLIS HONOR PRICE, B.Sc.

(Read at the Meeting, April 2, 1924.)

MITCHELL'S colorimetric method (ANALYST, 1923, 48, 2) for pyrogallol tannins has been in constant use in this laboratory for nearly a year, and, in view of the very satisfactory results obtained with it, I have, at the suggestion of Dr. Nierenstein, attempted to extend this method to the catechol tannins. The results have been disappointing, probably owing to the behaviour of the catechol nucleus in forming abnormal complex iron salts. (Cf. Weinland, *Einführung in die Chemie der Komplex-Verbindungen*, 1919.)

Although it was found that the method is satisfactory for the comparison of (1) Catechol with Catechol, (2) Protocatechuic Acid with Protocatechuic Acid and (3) Catechin with Catechin, yet the ratios which were obtained, on comparing these three substances with one another, were most unsatisfactory. This is shown by the results, some of which are given below. Unless otherwise stated, they were obtained from experiments carried out similarly to those described by Mitchell for the pyrogallol tannins, *i.e.* one c.c. of a 0.1 per cent. solution of the substance to be investigated was put into about 95 c.c. of water in a Nessler tube provided with a Hehner's side tubulure and tap, 2 c.c. of the reagent were added, and the solution was made up to 100 c.c. and compared with another solution prepared in like manner.

The water was estimated in each substance used and allowed for in the calculated ratios. These were obtained by taking the molecular weight ratios.

COMPARISON OF CATECHOL AND PROTOCATECHUIC ACID.—The calculated ratio is as follows:

$$\frac{\text{Catechol, } \text{C}_6\text{H}_4(\text{OH})_2, \text{ M.W. } 110}{\text{Protocatechuic acid, } \text{C}_6\text{H}_3(\text{OH})_2\text{.COOH} + \text{H}_2\text{O, M.W. } 172} = \frac{110}{172} = \frac{1}{1.56}$$

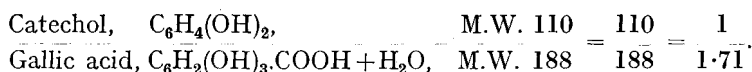
Calculated ratio in c.c. = 64:100. Found ratio in c.c. = 88.9:100, 88.1:100, 89.9:100, 88.8:100, 89.6:100, 89.9:100, 89.5:100, *93.7:100, 89.4:100, *94:100, 91.1:100 and *89:100.

Quite freshly prepared solutions, which standing could not have affected, gave the following ratios:—100:100, *100:96.3, *100:100 and 100:92.3.

A 0.1 per cent. catechol solution was compared with a 0.4 per cent. protocatechuic acid solution and the latter was diluted until the colours could be matched. Found ratio in c.c. = 89.2:100, 89.5:100, 89.6:100, 90.1:100, 91.5:100, 89.5:100, 87.7:100 and 89.8:100, when calculated for 0.1 per cent. solutions.

It is evident, therefore, that the ratio found when comparing catechol with protocatechuic acid is not a molecular one, as observed by Mitchell in the case of pyrogallol and gallic acid, where the carboxyl group acts as a diluent.

CATECHOL AND GALLIC ACID.—

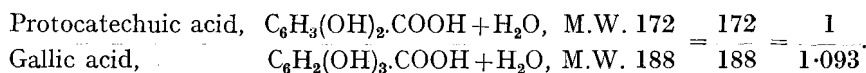


Calculated ratio in c.c. = 58.5:100. Found ratio in c.c. = 100:57.1, 100:57.1, 100:56.5, 100:57.6, 100:58.5, *100:44.8, 100:55.3, *100:52, 100:58 and *100:61.

For a 0.1 per cent. catechol solution compared with a 0.4 per cent. solution of gallic acid the found ratio in c.c. = 100:56, 100:51.3 and 100:50 calculated for 0.1 per cent. solutions.

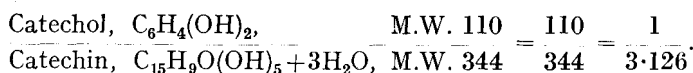
It should be noted that the ratio found is the reciprocal of the calculated one, which is strange.

PROTocatechuic ACID AND GALLIC ACID.—



Calculated ratio in c.c. = 91.5:100. Found ratio in c.c. = 100:57, *100:57, 100:61, *100:56, 100:55, *100:50, 100:51.9, *100:51.9, 100:51.9, 100:50.5, 100:51, *100:51.9, *100:51, 100:58.5, 100:60.7, and 100:59.4.

CATECHOL AND CATECHIN.—



Calculated ratio in c.c. = 100:312.5. Found ratio in c.c. = 100:213, 100:213, 100:199, 100:200, 100:195, 100:199, 100:200, 100:197, 100:193, 100:191, 100:213, 100:207, 100:210, 100:205, 100:211, and 100:213.

EXPERIMENTS WITH STANDARD SOLUTIONS AND MIXTURES.—According to the work on the pyrogallol nucleus, normal solutions of different substances should match each other if they behave similarly.

A 0.01 N solution of catechol was therefore compared with a 0.01 N solution of anhydrous catechin.

* These readings were taken by Miss W. N. Nicholson, B.Sc.

Calculated ratio in c.c. = 100:100. Found ratio in c.c. = 100:72.5, 100:72.4, 100:75.4, 100:67.4, 100:75.6, 100:75.5, 100:72.0, 100:73.5, 100:74.1, 100:75.0, and 100:74.6.

Equal volumes of 0.1 per cent. solutions of gallic and protocatechuic acids were mixed, and the resulting solution was compared first with gallic acid, and then with protocatechuic acid. The calculated ratios for these experiments were obtained from the one found above for protocatechuic and gallic acids.

$$\frac{\text{Gallic acid}}{\text{Protocatechuic acid}} = \frac{57.3}{100} = \frac{1}{1.744}$$

$$\text{Equal volumes mixed} = \frac{1 + 1.744}{2} = 1.372.$$

Therefore
$$\frac{\text{Gallic acid}}{\text{Mixture}} = \frac{1}{1.372}$$

Calculated ratio in c.c. = 74.8:100. Found ratio in c.c. = 73.0:100, 71.62:100, 74.11:100, 77.27:100, 73.16:100, 73.86:100, 72.88:100, and 74.0:100.

It is of interest to note that these values closely approach those required by theory, if the ratio chosen from which to calculate the theoretical result was correct.

$$\frac{\text{Protocatechuic acid}}{\text{Mixture}} = \frac{1.744}{1.372} = \frac{1.27}{1}$$

Calculated ratio in c.c. = 100:78.7. Found ratio in c.c. = 100:71.79, 100:72.05, 100:71.22, 100:68.0, 100:72.0, 100:71.34, 100:66.59, and 100:67.65.

$$\frac{\text{Pyrogallol, } C_6H_3(OH)_3 + 4.6 \text{ per cent. } H_2O, \text{ M.W. } 132}{\text{Catechol, } C_6H_4(OH)_2, \text{ M.W. } 110} = \frac{132}{110} = \frac{1.2}{1}$$

Calculated ratio in c.c. = 100:83. Found ratio in c.c. = 41:100, 40:100, 42:100, 45:100, and 43:100.

These readings were carried out jointly with Miss Nicholson. The last ratio was obtained with quite freshly prepared solutions.

A 0.01 *N* solution of pyrogallol was compared with solutions of catechol of various concentrations. The ratios varied as shown below. Since fresh pyrogallol solutions were not prepared each time, the variations are probably a measure of the oxidation of the pyrogallol nucleus. The results cannot, however, be used as a basis for calculation, since the readings were not taken at definite intervals.

Pyrogallol

Catechol

0.01 *N*:0.01 *N*. Expected ratio = 8:8. Found ratio = 3:8.

The following calculated ratios were obtained from the above found ratio:—

0.01 *N*:0.015 *N*. Calculated ratio = 4.5:8. Found ratio = 6:8.

0.01 *N*:0.02 *N*. Calculated ratio = 6:8. Found ratio = 8.8:8.

0.01 *N*:0.04 *N*. Calculated ratio = 12:8. Found ratio = 22.2:8.

The ratio 3:8 for 0.01 *N* solutions is theoretically 45:100 for 0.1 per cent. solutions as was found in one case given above. For pyrogallol against catechol the ratio 3:8 seems strange, since the ratio of the hydroxyl groups is 3:2. From these results, therefore, I am inclined to assume that 1 molecule of pyrogallol corresponds to 4 molecules of catechol.

From the above results it will be seen that with different substances the same ratio was rarely obtained twice following.

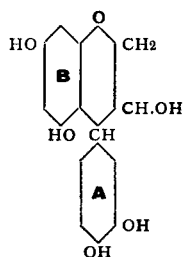
In each case the violet colorations had essentially to be of the same shade, or as nearly as possible the same, before the intensities could be compared. Many preliminary experiments were necessary for such an adjustment. Until all the substance which was present containing the catechol nucleus had been converted into the soluble ink, the addition of the reagent caused the amount of the violet colour to increase and thus the solution in the cylinder to darken, but once a sufficient quantity had been added, the addition of even a few drops more of the reagent turned the violet from a blue to a pink shade, probably due to the yellow colour of the reagent. With one solution slightly bluer than the other it was not easy to make correct estimations. The solutions were viewed vertically by daylight and by artificial light. If viewed horizontally, they looked very unlike.

The fact that the ratios $\frac{\text{Catechol}}{\text{Gallic acid}} = \frac{100}{57}$ and $\frac{\text{Protocatechuic acid}}{\text{Gallic acid}} = \frac{100}{57}$ were obtained is additional evidence showing that the carboxyl group in protocatechuic acid does not dilute the catechol nucleus.

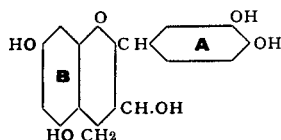
POSSIBLE EXPLANATION OF THE RATIOS.—Attempts were made to find explanations for the ratios obtained between the different substances in terms of the numbers of hydroxyl groups as well as the molecular weights. They were not, however, a success. This was also confirmed by the series of experiments kindly carried out by Miss Nicholson.

When comparing catechol with catechin it was found that the ratios varied very considerably according to the length of time the catechol solution had been standing. Fresh solutions, therefore, were absolutely necessary.

Experiments showed that a 0.01 *N* solution of catechin gives rise to a darker violet colour than a 0.01 *N* solution of catechol. Since catechin, according to the constitutional formula assigned to it by Nierenstein (*J. Chem. Soc.*, 1920, 117, 971), and also according to the Perkin and Freudenberg formula (*J. Chem. Soc.*, 1905, 87, 404; *Ber.*, 1920, 53, [B], 1416), contains the catechol nucleus A and the



Nierenstein's Formula.



Perkin and Freudenberg's Formula.

resorcinol nucleus B (which on opening in solution may lead to the formation of the phloroglucinol nucleus), it was thought that probably the additive effect between the nuclei A and B causes the darker colour. Attempts were therefore made to elucidate this point. Catechol was placed in each cylinder and resorcinol was added to one. Even 10 c.c. of 0.01 *N* resorcinol gave no change. Phloroglucinol acted similarly. Therefore the darker colour produced with the reagent by catechin is not due to the additive effect of the resorcinol or phloroglucinol nuclei.

THE GREEN COLORATION IN ACID SOLUTION.—A series of experiments was also carried out to find whether the catechol nucleus could be estimated in acid solution by using the green coloration produced.

The violet-coloured solutions were prepared as usual, and a small quantity of an acid solution (10 c.c. of glacial acetic acid in 90 c.c. of water) was added.

Protocatechuic acid	+0.3 c.c. of acid produced an apple-green colour.
Catechol	+0.3 c.c. of acid produced a yellowish-green colour.
Gallic acid	+1 c.c. of acid produced a greyish-green colour.
Pyrogallol	+1 c.c. of acid produced a greyish-green colour.

The green colour was very faint and of no use for comparisons. On diluting with tap water it turned bluish owing to the alkali in the water. When the solutions in the cylinders were made up with distilled water, and acid was added, a pale yellow colour was formed, but part of this was due to the yellow reagent. It seemed possible to tell by the shade of yellow whether any substance containing the pyrogallol nucleus or the catechol nucleus was present or not, and if so, which, but the amount could not be estimated.

EFFECT OF QUININE HYDROCHLORIDE.—In estimating gallotannin in the presence of gallic acid Mitchell uses quinine hydrochloride to precipitate the tannin. The most serious objection to this method for catechol tannins is, however, the fact that the presence of quinine hydrochloride (which is absolutely essential) with the reagent in a solution of catechol, protocatechuic acid or catechin causes precipitation. This does not occur with (1) the substance and quinine hydrochloride, (2) the substance and the reagent, or (3) the reagent and quinine hydrochloride, but only when all three are present together. Cinchonine sulphate solution acts similarly. On adding it to the violet solution a milky precipitate comes down immediately, which, in a few minutes, takes all the colour from the solution. On filtration a clear colourless filtrate is obtained, and a violet-coloured residue is left on the filter paper.

This definitely shows that the method cannot be applied to catechol tannins.

SUBSTANCES GIVING THE VIOLET COLORATION.—Mitchell, in his paper, says: "The reagent does not give any coloration with phenol or other mono-hydroxylated compounds, nor with salicylic acid or other compounds containing two hydroxyl groups. So far as my observations go, the violet colour is specific for the pyrogallic grouping."

It is interesting to note from a series of experiments which I have carried out that two hydroxyl groups in the *ortho* position are always necessary to get the violet coloration. Of the following substances investigated: phenol, hydroquinone, resorcinol, phloroglucinol, salicylic acid, meta-hydroxy-benzoic acid, β -resorcilic acid and guaiacol do not give the violet colour, whereas, catechol, protocatechuic acid, pyrogallol, gallotannin and gallic acid do give the violet colour.

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Estimation of Sugar in Urine by Means of Fehling's Solution with Methylene Blue as Internal Indicator.

BY J. HENRY LANE, B.Sc., F.I.C., AND LEWIS EYNON, B.Sc., F.I.C.

(Read at the Meeting, May 7, 1924.)

ABOUT a year ago we proposed the use of methylene blue as an internal indicator for Fehling's solution, and described a method of procedure for the exact volumetric determination of the more important reducing sugars (*J. Soc. Chem. Ind.*, 1923, 32T.; *ANALYST*, 1923, 48, 220). For sugar products we have found the method entirely satisfactory, but the case of urine stands somewhat apart, inasmuch as the greater part, if not the whole, of the reducing power of normal urine towards Fehling's solution is due to substances other than sugar, *e.g.* creatinine and uric acid. Methylene blue by itself in alkaline solution has been proposed for the detection of sugar in urine, although, according to Wender (*Chem. Zeit.*, 1893, 670), it is reduced by creatinine. Allen pronounced it very useful as a qualitative or limit test, but too sensitive to back-oxidation for exact quantitative purposes (*Chemistry of Urine*, p. 82). We find no reference to its use as an indicator for Fehling's solution, although the fact that it is decolorised by non-sugars present in urine would not necessarily impair its indicator action, provided that it retained its colour until all copper had been reduced.

If normal untreated urine is titrated against 10 c.c. of Fehling's solution in presence of methylene blue, by the incremental method described in our earlier paper (*loc. cit.*), no satisfactory end-point is obtained, because before all the copper is reduced the alkalinity of the Fehling's solution is so much diminished by the natural acidity of the added urine that the indicator cannot function properly. This difficulty can be overcome by first rendering the urine neutral to litmus. Operating on these lines with healthy urines we have found that 10 c.c. of Fehling's solution require about 40 to 70 c.c., corresponding to 0.12 to 0.07 per cent. of reducing matter calculated as dextrose, in the samples. In these titrations we

found it advisable to use 10 drops of the 1 per cent. methylene blue solution. The greater part of the colour of the indicator is discharged before the end-point is reached, but it is the disappearance of the last trace of greenish shade which marks the complete reduction of the copper, and after some practice this point can be determined to within 5 c.c.

In order to obtain a sharper end-point with these healthy urines we have tried defecation with normal lead acetate. This substance is widely used for the defecation of sugar products, since, unlike basic lead acetate, it does not remove any sugar from solution (*cf. J. Soc. Chem. Ind., 1923, 463T.; ANALYST, 1924, 49, 90*). It is necessary to remove the excess of lead from the defecated liquid, and for this purpose potassium oxalate is very suitable. To avoid dilution of the urine the reagents may be used in the dry state, the neutralised urine being first shaken for a minute or two with 3 grms. of powdered normal lead acetate per 100 c.c., then filtered through a dry filter and shaken for a minute with 1 grm. of powdered potassium oxalate per 100 c.c., and again filtered. Experiments on urines have shown that this treatment does not remove any reducing sugar. It does remove a small quantity of reducing non-sugars, equivalent in reducing power to about 0.02 to 0.03 per cent. of dextrose, so that the percentage of sugar found after defecation will be nearer by this amount to the true value than that found without defecation. Such a small difference, however, is practically negligible, and the only advantage of defecation with normal lead acetate is that it renders the urine much lighter in colour and makes the end-point of the titration more distinct. This is an advantage in the titration of urines of low reducing power, corresponding to about 0.2 per cent. or less of dextrose, but when the reducing power rises to values of pathological significance, and the urine has to be diluted before titration against 10 c.c. of Fehling's solution, the end-point can be recognised without difficulty, whether the urine is defecated or not. The higher the percentage of sugar in a urine, the more does it need to be diluted before titration, and the greater becomes the precision of the titration, since the interfering non-sugars are correspondingly diluted. As the sugar-content of the urine rises beyond 1 or 2 per cent., the degree of precision approaches that attainable with pure sugar solutions, which is of the order of 0.2 per cent. of the amount of sugar estimated.

On the basis of these observations we propose the following method of testing urines for sugar. It has the advantage of starting with a sort of limit test, which is very simple to carry out, and beyond which it is not necessary to go if the reducing power corresponds with that of normal urines. It is essential that the sample should first be rendered neutral if it is acid; addition of 1 c.c. of a 10 per cent. solution of sodium hydroxide per 100 c.c. of urine is usually sufficient, and, if necessary, the sugar-content found must be corrected for this dilution. Defecation with normal lead acetate may be carried out as described above, but is not essential. Ten c.c. of Fehling's solution (Soxhlet's modification, containing 34.64 grms. of crystallised copper sulphate, 173 grms. of Rochelle salt and 50 grms. of sodium hydroxide per litre) in a flask of about 300 c.c. capacity are treated with 20 c.c. of the neutralised urine and heated to boiling over a wire gauze. It is a good plan

to introduce a trace of vaseline on the end of a glass rod into the liquid, to prevent excessive frothing at a later stage. When the liquid has been boiling for a minute 10 drops of a 1 per cent. aqueous methylene blue solution are added (preferably without touching the sides of the flask) and boiling is continued. If the methylene blue is completely decolorised within about 15 seconds, so that the reaction liquid appears exactly as before the addition, the urine contains more than 0.25 per cent. of reducing matter calculated as dextrose, and to estimate the amount a fresh titration must be carried out with the urine suitably diluted. If, on the other hand, as is usually the case with normal urines, the methylene blue is not completely decolorised, the amount of reducing substances is less than 0.25 per cent., and, if it is necessary to estimate their amount, the titration is continued by adding 10 or 5 c.c. increments of urine to the boiling liquid in the flask, with about 15 seconds' actual ebullition after each addition, until all trace of greenish tint has disappeared. For the estimation of such small quantities of reducing substances it may be taken that 10 c.c. of Fehling's solution correspond to 0.05 gm. of dextrose.

In cases where this preliminary test shows more than 0.25 per cent., and the titration has to be repeated after suitable dilution of the sample, the procedure described in our earlier paper (*loc. cit.*) may be followed. Ten c.c. of Fehling's solution are treated with 15 c.c. of the diluted urine in a flask of about 300 c.c. capacity and heated to boiling over a wire gauze, and further additions of urine are made at intervals, with about 15 seconds' actual ebullition after each, until almost all the copper appears to be reduced, whereupon 3 to 5 drops of the indicator solution are added, and the addition of urine is continued in small increments until the indicator is completely decolorised. If the maximum accuracy is desired, it is advisable to repeat the titration by our standard method (*loc. cit.*), 10 c.c. of Fehling's solution being boiled for 2 minutes with almost the whole volume of diluted urine required for its reduction, after which 4 drops of indicator are added and the titration is completed in 1 minute further. The results are interpreted by means of the dextrose table given in our earlier paper and reproduced here (Table I.).

TABLE I.

Dextrose Table for 10 c.c. of Fehling's Solution.

Sugar solution required. c.c.	Anhydrous dextrose corresponding to 10 c.c. of Fehling's solution. Mgrms.	Anhydrous dextrose per 100 c.c. of sugar solution. Mgrms.
15	49.1	327
16	49.2	307
17	49.3	289
18	49.3	274
19	49.4	260
20	49.5	247.4
21	49.5	235.8
22	49.6	225.5
23	49.7	216.1
24	49.8	207.4

TABLE I.—(continued).

Sugar solution required.	Anhydrous dextrose corresponding to 10 c.c. of Fehling's solution.	Anhydrous dextrose per 100 c.c. of sugar solution.
c.c.	Mgrms.	Mgrms.
25	49.8	199.3
26	49.9	191.8
27	49.9	184.9
28	50.0	178.5
29	50.0	172.5
30	50.1	167.0
31	50.2	161.8
32	50.2	156.9
33	50.3	152.4
34	50.3	148.0
35	50.4	143.9
36	50.4	140.0
37	50.5	136.4
38	50.5	132.9
39	50.6	129.6
40	50.6	126.5
41	50.7	123.6
42	50.7	120.8
43	50.8	118.1
44	50.8	115.5
45	50.9	113.0
46	50.9	110.6
47	51.0	108.4
48	51.0	106.2
49	51.0	104.1
50	51.1	102.2

The results obtained with the method described above agree closely with those given by Gerrard's cyano-cupric method, but are considerably lower than those obtained with Pavy's method. The higher results given by the latter method are to be attributed to the non-sugars, as is indicated by the figures in Table II.

TABLE II.

Sugar Estimations in Urine.

By means of Fehling's Solution with Methylene Blue Indicator.				By means of Pavy's Solution.			
Original reducers as dextrose R.	Added dextrose D	R + D	Total found.	Original reducers as dextrose R'.	Added dextrose D.	R' + D	Total found.
Per Cent.	Per Cent.		Per Cent.	Per Cent.	Per Cent.		Per Cent.
0.12	0.10	0.22	0.21	—	—	—	—
0.09	0.29	0.38	0.38	0.17	0.29	0.46	0.47
0.09	0.57	0.66	0.67	0.17	0.57	0.74	0.75
0.10	1.45	1.55	1.59	0.19	1.45	1.64	1.64
0.10	2.90	3.00	3.00	0.19	2.90	3.09	3.27

referring to comparative estimations by Pavy's and our methods. All the figures in the same horizontal line relate to the same sample of normal urine, neutralised, defecated with normal lead acetate and freed from lead by means of potassium oxalate, without and with addition of a known quantity of dextrose. The Pavy's solution used contained per litre: 4.158 grms. of crystallised copper sulphate, 20.4 grms. of Rochelle salt, 20.4 grms. of potassium hydroxide, and 300 c.c. of concentrated ammonia; 40 c.c. were used for each titration and taken as equivalent to 0.02 gm. of dextrose.

It is clear from the table that Pavy's method gives higher values than ours for the reducing substances of normal urine, and as these substances consist chiefly, if not entirely, of non-sugars, this is a point in favour of the new method. Allowing for these differences in the original reducer-content, the results for the added dextrose are practically the same by both methods. For large amounts of sugar our method is much more accurate than Pavy's, since the end-point can be determined with greater precision by the former. In the estimation of sugar in urine, however, extreme accuracy is, in many cases, not essential, and the chief practical advantages of the new method over Pavy's are its greater convenience and cheapness, and the avoidance of ammoniacal vapours.

It may be of interest to mention that methylene blue can be used as an internal indicator in Pavy's solution. It does not act quite so readily as it does in Fehling's solution, but it sharpens the end-point, especially in the case of coloured liquids. If it were employed in this way for accurate work, it would be necessary to add always the same amount of indicator and to standardise the method against dextrose, as the end-point, although fairly sharp, comes somewhat later than when Pavy's solution is used without an indicator.

DISCUSSION.

Mr. A. CHASTON CHAPMAN said that, speaking from his own experience, he was inclined to give preference to the method of Pavy.

Mr. WM. PARTRIDGE said that accuracy in sugar estimations was very important in cases of diabetes where patients were being kept alive largely by the skill in dieting by the doctor. In such cases the useful figure was, not the percentage, but the actual amount, of sugar passed per diem. In his opinion Fehling's solution was not always reliable for urine, but was most useful when used gravimetrically. The most accurate method of estimating sugar in urine was to take the gravity, ferment with washed yeast, and take the gravity again.

Mr. C. L. CLAREMONT enquired whether the authors found differences in samples of methylene blue. In his experience the German product contained a good deal of methylene mauve. He asked whether there were different varieties of methylene blues, as it seemed to him they varied with different firms.

Mr. JOHNSON asked the authors if they would give their reasons for using this special table of equivalents for their estimations.

Mr. G. R. THOMPSON thanked the authors for their novel contribution and asked whether they had experimented with this method with abnormal urine. In his opinion, the potassium iodide method was a good one, in that with morphine present there would be no interference. He considered the Fehling's solution method a more desirable one than Pavy's method.

Mr. L. EYNON, in reply, said that the gravimetric method suggested by Mr. Partridge was slow and troublesome, and not so good as the volumetric method with an internal indicator. They had not found variation in samples of methylene blue, such as Mr. Claremont mentioned, although one sample had been unsatisfactory. The table in the paper, referred to by Mr. Johnson, was one published in the Journal of the Society of Chemical Industry, which had been prepared with great care and gave good results. They had not tried any abnormal samples of urine; they had worked with normal urine to which dextrose had been added. The effect of morphine had not yet been worked out, and they were unable to say what it would be.

The Estimation of Copper and Tin in Copper-Tin Alloys.*

By A. T. ETHERIDGE, M.B.E., B.Sc., F.I.C.

(Read at the Meeting, May 7, 1924.)

THE common method of separating tin as stannic oxide by the action of nitric acid has many disadvantages. The stannic oxide occludes practically every other metal in the alloy, as well as phosphorus from phosphor bronze, and the total amount of impurity may be from 5 to 10 per cent. It has been found well-nigh impossible to decompose the impure oxide at one fusion, the difficulty apparently increasing with increase of temperature of ignition. Moreover, the assumption that the sulphides, after ignition, can be considered to be oxides is not correct, and introduces an error in the estimation of tin by difference; also the separated sulphides are apt to retain tin, which is difficult to wash out, and leads to low results if the attempt is made to estimate tin directly. It has also been found that the crucibles, necessarily of porcelain, are severely injured by the fusion, even when carried out carefully over a small flame. Variations in the initial nitric acid attack have been suggested as a means of diminishing occluded impurities, but, in my experience, these have not produced a pure stannic oxide.

The special case of phosphorus from phosphor bronze is well known. It is assumed that all the phosphorus is present in the precipitate as P_2O_5 , and an allowance is made after the phosphorus has been estimated; or, alternatively, the tin is estimated directly as mentioned above.

For these reasons the author has long discarded the nitric acid treatment in favour of a new method worked out after numerous experiments. The principle of the new method is to separate copper from a sulphuric acid solution by electrolysis, the conditions being such that the tin is held completely in solution, and is not precipitated by hydrolysis. This method of separation is not referred to in any books dealing with electro-analysis, as apparently it has not been realised that copper can be separated quantitatively from strongly acid solutions.

* Communication from the Research Department, Woolwich.

The details of the method are as follows:—One gram. of the alloy (or 0.5 gram. if the tin exceeds 10 per cent.), preferably drillings or turnings (freed from iron particles by a magnet) is dissolved in a mixture of 60 c.c. of dilute sulphuric acid (one vol. of conc. acid to three vols. of water) and 5 c.c. of nitric acid (sp. gr. 1.42) in a 400 c.c. squat beaker. If the solution is quite clear it is diluted to 200 c.c. and electrolysed. If a gelatinous residue is observed it is an indication of phosphorus or arsenic or both, probably as stannic phosphate or arsenate. If lead is present a dense white precipitate of lead sulphate will be observed, and this masks any other residue which may be there. In either case it is necessary to evaporate the solution carefully until it fumes, after adding about 20 c.c. more dilute sulphuric acid, to allow for sulphuric acid lost by evaporation. This treatment decomposes the stannic phosphate (or arsenate) and also allows lead to be quantitatively separated in the next operation. After cooling down to room temperature, about 150 c.c. cold water are quickly added, and the liquid is well shaken, to prevent local overheating. Excessive heating would cause separation of tin as hydrate by hydrolysis, and this would necessitate evaporating again or starting afresh. A clear liquid at this stage indicates absence of lead. Any lead sulphate separates rapidly as a heavy white precipitate and can be filtered off after the beaker has stood for about 30 minutes in cold running water. The lead is estimated in the usual way. If it is small in amount, say not more than 2 or 3 per cent., there is no danger of loss of copper or tin by occlusion. After the lead sulphate has been washed the volume of the filtrate is approximately 200 c.c. and, having been caught in a 400 c.c. beaker, is ready for electrolysis after the addition of 10 c.c. of nitric acid (sp. gr. 1.2) or 5 c.c. of colourless nitric acid (sp. gr. 1.42). The addition of nitric acid in small amounts is necessary in order to obtain a good copper deposit in the subsequent electrolysis. Of course no further nitric acid need be added if the alloy dissolves completely in the initial acid mixture. If tin separates by hydrolysis on standing, or during electrolysis, it is an indication of insufficient sulphuric acid, and a fresh start must be made, more acid or less alloy being used, or more allowance made for evaporation.

SEPARATION OF COPPER BY ELECTROLYSIS.—A rotating cathode of platinum gauze is used with a small platinum foil anode. There is nothing quite so satisfactory as platinum for the cathode. The gauze form is not absolutely essential, but it is necessary to have the cathode rotating (or the liquid stirred) on account of the heavy currents used. If the cost is prohibitive platinum might be replaced by silver. In that case the copper is subsequently removed by an ammonia solution of trichloroacetic acid (*J. Amer. Chem. Soc.*, 1921, 43, 700). A platinum anode is essential, but is so small that it is comparatively inexpensive. A current of 4 amps. is used, from a 10 or 20 volt circuit, provided with a rheostat of such a resistance that the current can be lowered to 0.5 amp. or less. After the current has been on 30 minutes, about 0.5 gram. of urea is added to destroy any nitrous acid developed by the current. (Nitrous acid tends to delay the copper deposit.) When the liquid has become apparently free from copper the same current is continued for a further 30 minutes. Hydrogen is often generated at this stage in large volumes, but

has no effect on the deposit. At the end of this time the current is reduced by 0.5 amp. every 15 minutes, down to the final stage of 0.5 amp. At each change 0.5 gm. of urea is added.

The sides of the beaker and the exposed platinum are washed from time to time with the wash-bottle jet, and finally the beaker is lowered away from the cathode, with the current left on, and the cathode washed at the same time with the wash bottle jet. The cathode is now detached, washed with alcohol, dried in a low-temperature oven, and weighed. The initial treatment of the cathode, after ignition in a muffle, having been the same, the difference in weight represents the copper in the alloy weight taken.

The cathode must not be allowed to stand wet in the air. It should be dipped into alcohol as soon as it is washed. A good colour of the deposit indicates freedom of the alloy from antimony and bismuth, which metals are, to some extent, deposited with copper. Unusually large amounts of either would completely blacken the copper and render the method useless, but traces, which cause slight discoloration only, can be ignored. Bronzes of high quality give an extremely pure copper, whilst ordinary commercial bronzes of medium quality nearly always give some discoloration. If the discoloration is too bad to be ignored the analyses would have to be abandoned and the alloy treated in an entirely different way, as described under the heading of analysis of copper-antimony (or bismuth)—tin alloys. The author has not come across any bronzes of this kind, however, and the possibility of encountering them appears to be remote.

ESTIMATION OF TIN.—The anode is now washed and removed. (Slight traces of lead peroxide may occasionally be observed on the anode, usually from alloys which have dissolved completely in the initial acid mixture, indicating traces of lead in the alloy). The tin is precipitated as stannic sulphide by the passage of a rapid current of hydrogen sulphide about 30 minutes. The precipitate is allowed to stand some time, preferably overnight, before filtering. It is best filtered through ashless pulp, and washed with dilute ammonium nitrate solution. Washing with water tends to carry some of the precipitate through the filter.

The precipitate is transferred to a porcelain crucible, previously covered with a layer of ashless paper, to prevent contact of the sulphide with the porcelain.

Ignition is carried out for some time at a low heat (below dull red), preferably first in a low temperature muffle, and is afterwards completed in a high temperature muffle at the usual red heat. In this way stannic sulphide can be completely converted into oxide. The precipitate is brushed out, when cold, into a counter-poised aluminium scoop and weighed.

Unless the precipitate is unusually large it is not contaminated with iron or any other metals, such as zinc or nickel. These are easily washed out, but, if the precipitate is too large, it is better to start again with 0.5 gm. of alloy. Contamination with antimony and bismuth is possible, as these are only partly deposited with copper, but their presence will have been detected, as mentioned, by the colour of the copper deposit. Traces can be ignored.

Cadmium is seldom present in bronzes, but is sometimes met with in brasses,

e.g. Admiralty brasses with 1 per cent. tin. These alloys (of which 2 grms. is a convenient weight to use, with 7 c.c. of 1.42 nitric acid instead of 5 c.c.) might contain cadmium which would contaminate the tin, although the author has not met with such a case. If it is present to the extent of, say, 0.1 per cent., the precipitate of stannic sulphide should be extracted with sodium sulphide, filtered after standing, and the tin reprecipitated.

Arsenic may be in the solution and is then precipitated with the tin. It appears, however, to be completely volatilised by the method of ignition described. No interference with the method has been observed in the case of bronzes containing 0.5 per cent. of arsenic, most of which may, conceivably, be removed as hydrogen arsenide at the cathode, during electrolysis. It is not deposited on the cathode under the conditions used in this process.

The complete removal of copper from solution by the method given is certain. If any black turbidity is observed when the hydrogen sulphide is first introduced it is an indication that copper is present and that the conditions for electrolytic separation have not been correct, and a fresh start must then be made.

The filtrate from the stannic sulphide is used for estimation of iron, nickel, zinc, etc. Alternatively the filtrate can be used for the estimation of phosphorus, if desired, but this is seldom convenient since 2 grms. is usually the best amount to take. Also, it is quicker to separate copper and tin together as sulphide from hydrochloric acid solution in one operation, and to use the filtrate for the estimation of phosphorus.

DISCUSSION.

Mr. J. MYERS, referring to a remark in the early part of the paper that stannic oxide occluded every other metal, said that this was undoubtedly a source of error in the usual method of separating tin. The author had devised a method which involved a sharp separation, and he would like to congratulate him on a serious and successful effort to overcome a constantly occurring difficulty in metallurgical analysis.

He had looked with some suspicion upon the separation of tin with hydrogen sulphide in the presence of nitric acid, which had been generally considered an unsafe method, but, upon making trial with similar solutions both in presence and absence of nitric acid, and also in presence of arsenic, his results were all in excellent agreement with control tests, where tin was reduced with antimony and titrated with iodine. He was satisfied on this point and very much pleased with the method. If the author had details of results obtained by one or other of the well known volumetric methods applied to tin in a sample of bronze, together with results by the new method, the figures would be both interesting and of value in furnishing a comparison of the degree of accuracy which could be obtained by the older methods.

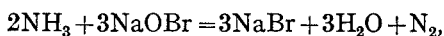
Mr. W. H. WOODCOCK said he was much interested in the paper, but was surprised to hear this was put forward as a new process, for it was one he had used for over 20 years. Regarding the problem of current for electro-deposition, it was possible to get over the difficulty by using an ordinary power main with a lamp resistance, and leaving it running all night; copper could be obtained by this means quite pure; it was usual to oxidise tin sulphide to stannic acid.

Mr. G. RUDD THOMPSON said that, in his opinion, it was absolutely necessary to use platinum for the electrolytic deposition of copper, but silver could be used with other metals.

The Estimation of Ammonia by Means of Sodium Hypobromite.

BY MAXWELL BRUCE DONALD, M.Sc., A.R.C.Sc., A.I.C.

EARLY workers in this field generally used brominated solutions of sodium hypochlorite; these are not only difficult to prepare accurately, but also lead to the formation of by-products such as hydrazine, J. Thiele (*Annalen*, 1893, **273**, 160), and possibly nitrogen trichloride, W. A. Noyes and A. C. Lyon (*J. Amer. Chem. Soc.*, 1901, **23**, 460). The use of sodium hypobromite appears to have been first suggested by W. Knop (*Zeitsch. anal. chem.*, 1870, **9**, 225), and the reaction is generally represented as:



notwithstanding the fact that there is no evolution of nitrogen if ammonia and pure sodium hypobromite are mixed. The evolution of gas only occurs when there is an excess of the sodium hydroxide above that required to form hypobromite. The reaction is probably very similar to the Hofmann reaction (*Ber.*, 1882), in which a brominated compound is formed, which is then decomposed by alkali.

A few qualitative experiments show that the rate of evolution of nitrogen increases with the amount of free sodium hydroxide present, indicating that the rate of decomposition of the brominated compound is dependent on the amount of alkali available for its decomposition.

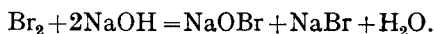
This reaction can be used for the analysis of ammonium compounds in two ways; either by measuring the amount of nitrogen evolved or by estimating volumetrically the amount of hypobromite unacted upon.

The amount of nitrogen evolved is short of the correct amount, the deficit depending on the nature of the hypobromite solution and the method of collecting the gas. Thus, using a 40 per cent. brominated 10 *N* sodium hydroxide solution, Dietrich (*Zeitsch. anal. chem.*, 1867, **5**, 36) had a deficit which varied from 2 to 3 per cent., and W. Foster (*J. Chem. Soc.*, 1878, **33**, 470) one of 7 per cent., whilst A. Wohl (*Ber.*, 1903, **36**, 1418), using 50 per cent. brominated 1.5 *N* sodium hydroxide solution had a deficit of 4.8 per cent.

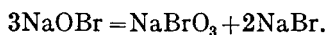
The amount of hypobromite which has been unacted upon can be estimated by the method that H. J. Hamburger (*Zeitsch. f. Biol.*, 1885 [3], **20**, 286) used for urea, *i.e.* adding excess of sodium arsenite and titrating this excess by means of a standard solution of iodine in potassium iodide. This method has been tried by D. R. Nanji and W. S. Shaw (*ANALYST*, 1923, **48**, 473), who found that it gave too high results for ammonium chloride.

Another method of estimating the excess of sodium hypobromite is by acidifying, adding potassium iodide, and titrating the iodine liberated with sodium thiosulphate; this was employed by E. Rupp and E. Rössler (*Arch. Pharm.*, 1905, **243**, 104). They state that for estimating ammonia which contains only a small amount of free alkali it is best to use a hypobromite. The solutions which they used to prove this point were 38 per cent. brominated 2 *N* sodium hydroxide solution and 85 per cent. brominated *N* sodium hydroxide solutions, but the figures that they quote in support are not convincing. H. H. Willard and W. E. Cake (*J. Amer. Chem. Soc.*, 1920, **42**, 2646) used this method to determine the nitrogen converted into ammonia by the Kjeldahl process with accurate results. A very accurate estimation was made by P. Artmann and A. Skrabal (*Zeitsch. anal. Chem.*, 1907, **46**, 5), who obtained good results for various ammonium salts by using 50 per cent. brominated *N* sodium hydroxide solutions.

The reason why the sodium arsenite method gives results which are too high is probably due to reactions which occur in the hypobromite. If bromine is added slowly to a well-cooled solution of sodium hydroxide, the reaction which takes place is as follows:



If, however, the temperature is allowed to rise, some of the hypobromite is converted into bromate:



The hypobromite can also break down directly, giving off oxygen gas, especially if traces of a salt of copper, nickel or cobalt are present, but P. Fleury (*Compt. rend.*, 1920, **171**, 957) has shown that this reaction can be inhibited by adding 0.1 per cent. of potassium iodide to the solution.

It has been shown by F. A. Gooch and J. C. Blake (*Amer. J. Sci.*, 1902 (4), **14**, 285) that arsenious acid is only oxidised quickly by bromates in strongly acid, boiling solutions. At ordinary temperatures the reaction requires about an hour for completion, and therefore it is possible that in sodium bicarbonate solution the reaction will not occur at all. Experiments were made by adding sodium bromate solution to sodium arsenite, and then adding sodium bicarbonate, but no reaction could be detected, and the amount of iodine required for a given quantity of sodium arsenite remained constant until the solutions were acidified and heated on the steam bath.

The fact that the sodium arsenite method gives high results may be due to the fact that the reaction between ammonia and hypobromite causes some of the latter to be converted into bromate, and this hypobromite will therefore not appear in the second titration. Gooch and Blake also show that the reaction between acidified bromate and potassium iodide does not quite go to completion, but, as there is very little bromate in the original hypobromite and, also, as two minutes are allowed before titrating with thiosulphate, this error is negligible.

EXPERIMENTAL.

Ammonium chloride.—The ammonium chloride used was Kahlbaum's "Zur Analyse," with guarantee, which had been dried at 105° C.; 1.6 gm. was dissolved in distilled water and the solution made up to one litre, so that 10 c.c. were equivalent to 4.193 mgrms. of nitrogen.

Sodium thiosulphate.—This was standardised by means of potassium dichromate and potassium permanganate and found to be 0.06132 *N*.

Sodium hypobromite.—This was made of a similar strength to that used by Nanji and Shaw by dissolving 2 grms. of sodium hydroxide in two litres of distilled water, which was then cooled in a freezing mixture and 3.4 grms. of bromine slowly added. This procedure ensures that a minimum amount of bromate is formed. The solution was allowed to attain room temperature just before it was required. The strength of this solution was therefore 85 per cent. brominated 0.025 *N* sodium hydroxide solution.

Since it was found that, as the amount of free sodium hydroxide is decreased, the reaction takes more time for completion, the procedure was to add the ammonium chloride solution slowly to the hypobromite in a litre flask (not *vice-versa*) and, after being well shaken, it was allowed to stand for five minutes. The solution was then acidified with hydrochloric acid, and a solution of about 3 grms. of potassium iodide in water added. Sufficient water was added to bring the volume up to 250 c.c., and the iodine was then titrated with thiosulphate after waiting for about 2 minutes to allow the traces of bromate to react completely with the potassium iodide. The results obtained are shown in Table I.

TABLE I.

NaOBr. c.c.	Excess. Per Cent.	Thiosulphate, before. c.c.	Thiosulphate, after. c.c.	Thiosulphate used. c.c.
50	9.2	16.09	1.37	14.72
100	119	32.16	17.44	14.74
100	119	32.18	17.42	14.76
150	228	48.24	33.52	14.72
150	228	48.24	33.46	14.78
200	337	64.34	49.62	14.72
200	337	64.34	49.65	14.69
			Mean	14.73

$$14.73 \times 0.02044 \times 14.008 = 4.217 \text{ mgrms. of nitrogen.}$$

As the value obtained was about 0.6 per cent. too high, a fresh estimation was made, the ratio of bromine to sodium hydroxide recommended by Artmann

and Skrabal (*i.e.* 50 per cent. brominated 0.025 *N* sodium hydroxide solution) being used. These results are given in Table II.

TABLE II.

NaOBr. c.c.	Excess. Per Cent.	Thiosulphate, before. c.c.	Thiosulphate, after. c.c.	Thiosulphate used. c.c.	
50	—	9.42	—	—	
100	28.5	18.87	4.19	14.68	
100	28.5	18.83	4.18	14.65	
150	92.6	28.26	13.60	14.66	
150	92.6	28.26	13.60	14.66	
				Mean	14.66

$14.66 \times 0.02044 \times 14.008 = 4.198$ mgrms. of nitrogen, or an error of about 0.1 per cent.

These results show that, providing the procedure detailed above is followed, the estimation of ammonia by means of sodium hypobromite is a very accurate method.

In order to compare this method with the arsenious oxide method of Nanji and Shaw experiments were made, with the following results:

Thiosulphate = 0.06132 *N*.

20.00 c.c. iodine in KI = 12.81, 12.81, mean: 12.81 c.c. thiosulphate.

5 c.c. sodium arsenite = 12.65, 12.64, mean: 12.65 c.c. iodine.

25 c.c. NaOBr + 10 c.c. As₂O₃ = 11.42, 11.42, mean: 11.42 c.c. iodine.

25 c.c. NaOBr + HCl + KI = 8.96, 8.95, Mean: 8.96 c.c. thiosulphate.

Hypobromite by arsenious oxide method = 0.02180 *N*.

Hypobromite by thiosulphate method = 0.02197 *N*.

50 c.c. NaOBr + 10 c.c. NH₄Cl + 5 c.c. As₂O₃ = 6.24, 6.50, 6.74, 7.16, 7.06 c.c. iodine, corresponding to 3.91 to 4.08 mgrms. of nitrogen and about 22 per cent. excess of hypobromite.

The ammonium chloride was checked against some twice re-crystallised ammonium chloride from another source, and the two gave identical results when acidified and titrated with thiosulphate after adding potassium iodide.

SUMMARY.—(1) The most accurate method of estimating ammonium salts by means of sodium hypobromite is a modification of that used by Artmann and Skrabal.

(2) Small quantities of ammonia corresponding to 4 mgrms. of nitrogen can be estimated by means of 50 per cent. brominated sodium hypobromite solution with an accuracy of about 0.1 per cent.

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.

A QUALITATIVE DIFFERENTIATION BETWEEN CUBE GAMBIEER AND INDIAN CUTCH.

IT has frequently been noticed in this laboratory that whereas cube gambier gives a green-coloured extract on boiling with chloroform, no such coloration is obtained when authentic Indian cutches are treated in the same manner.

Since cube gambier is prepared from the leaves of *Uncaria Gambier*, whereas the Indian cutches are prepared from the heart-wood of *Acacia catechu*, *A. catechuoides* and *A. sundra*, it seemed possible that the green coloration of the chloroform extract was due to chlorophyll. I have, at the suggestion of Dr. Nierenstein, investigated cube gambier, and have found that the chloroform extract contains chlorophyll.

About 1 gm. of cube gambier was heated for a short time on a boiling water bath with 10 c.c. of chloroform, and the filtered solution examined in a direct vision spectroscope, when a distinct spectrum, corresponding to that of chlorophyll, was obtained.

The test is fairly delicate, as will be seen from the following experiments:

Cutch. gm.	Chloroform. c.c.	Colour of Extract.	Remarks.
2	7	dark green	Definite chlorophyll spectrum.
1	7	dark green	Definite chlorophyll spectrum.
0.5	7	pale green	Faint spectrum.
0.3	7	pale green	Chlorophyll not detectable.
0.2	7	yellowish	Chlorophyll not detectable.

From the results of these experiments I would suggest using 1 to 2 grms. of cube gambier and 7 to 10 c.c. of chloroform for the detection of chlorophyll in cube gambier. In this connection it must be mentioned that one of the cube gambier specimens examined gave a good chlorophyll spectrum when only 0.3 gm. of it was extracted with 7 c.c. of chloroform.

None of the Indian cutches examined answered to this test, which can therefore be used as a method for the differentiation of cube gambier from Indian cutches. This is of importance, as it is known that adulterated gambier cutches are placed on the Deccan markets as genuine Indian cutches. (Cf. D. Hooper, *Indian Agricultural Ledger*, 1906, p. 44.)

R. P. BIGGS.

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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.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE 1ST QUARTER, 1924.

DURING the quarter, 1456 samples were examined, of which 1264 were submitted under the Sale of Foods and Drugs Acts, 1077 being bought informally (of which 51 were adulterated), and 187 bought under the provisions of the Acts (of which 20 were adulterated).

MILK.—Of the 669 samples examined, 45 were reported as adulterated.

CONDENSED MILK.—Only one of 4 informal samples of full cream sweetened condensed milk was satisfactory. One contained 8.7 per cent., and a second 8.8 per cent. of fat, instead of the minimum 9 per cent., whilst the directions for diluting the third sample did not appear to comply with the regulations. In each case the manufacturer was cautioned.

MUSTARD.—Sixteen samples were genuine, but two, bought at one shop, contained about 28 per cent. of potato starch and turmeric.

GROUND GINGER.—Ten samples were genuine, and 4 adulterated. Two of these (a formal and an informal sample from the same vendor) contained about 2 per cent. of chalk. Two other samples (formal and informal) from the same vendor were deficient in soluble pungent principles. The formal sample contained 3.0 per cent. of ash, of which 1.80 per cent. was soluble in water, and 0.34 per cent. insoluble in acid. The cold water extract was 6.6 per cent. The average composition of 250 samples of ground ginger purchased in Birmingham during the past 30 years was as follows:—Ash, 5.34 per cent., of which 2.54 per cent. was soluble in water, and 0.63 per cent. insoluble in acid. Cold water extract 12.7 per cent. The two owners of the shop were each fined 5s.

CUSTARDS.—Nine samples were free from boric acid. Three, examined in detail, consisted on the average of 36 per cent. of custard and 64 per cent. of pastry. The average percentage composition was as follows:

	Custard.	Pastry.	Total.
Protein	8.4	5.6	6.6
Fat	8.3	16.9	13.8
Ash	1.0	0.4	0.6
Moisture	67.9	35.2	47.0
Starch, etc.	14.4	41.9	32.0
Nitrogen	1.29	0.87	1.01

ALE.—One informal sample and one formal sample from one vendor contained chlorides equivalent to about 100 grains of salt per gallon, and the vendor was cautioned.

PURE SULPHATE OF IRON.—The pure chemical contains 45.4 per cent. of moisture, some of which is lost on exposure to the air, so that the drug becomes

stronger. The B.P. requires the salt to be crystalline and of a greenish colour. Before 5 per cent. of moisture is lost the drug becomes white and powdery, and would not comply with the B.P. requirements. Six informal samples contained the equivalent of 100.3 to 101.5 per cent. of pure ferrous sulphate, and were passed as genuine. About 1 oz. of the granular sulphate was kept in an open bottle for 28 days, and during that period lost 1.9 per cent. of moisture. When freely exposed to the air, 9 samples lost from 18.0 to 20.4 per cent. of moisture in about 12 days and showed no further loss. This amount corresponds to about 3/7 of the water of crystallisation.

QUININE SULPHATE.—None of the six informal samples contained 15.2 per cent. of water—the amount implied in the composition of the salt as stated in the B.P.—the percentage varying from 4.6 to 12.0. It is suggested that the statement in the B.P., that quinine sulphate loses water of crystallisation, is not intended to justify the use of such an indefinite substance. It is probable that this tendency of quinine sulphate to become stronger through loss of water will account for the fact that dispensed mixtures containing quinine sulphate have been found too strong, and also for the excess of quinine found in B.P. preparations, such as ammoniated tincture of quinine.

J. F. LIVERSEEGE.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

COMPOUND CASTOR OIL TABLETS.

ON April 14th a druggist was charged at the Magistrate's Court, Wanganui, New Zealand, with selling a drug in a package, to wit, compound castor oil chocolates, bearing and having attached thereto a false or misleading statement. The analyst's report stated that "the material was in a form of chocolate coloured tablets of an average weight of 1.55 grms., and contained matter soluble in petroleum spirit 4.4 per cent., phenolphthalein, 7 per cent. Not more than half the matter soluble in petroleum spirit was castor oil, and it was possible that no castor oil was present. Assuming that the material contained 2.2 per cent. of castor oil, 116 tablets would be required to provide a minimum dose of that substance. The dose prescribed for a child of three to ten years was one tablet. It was evident, therefore, that the quantity of castor oil present would not have the slightest medicinal action. The active ingredient was the phenolphthalein. The statement "Compound Castor Oil Tablets" appearing on the original package was misleading, and in contravention of Sec. 12 of the Sale of Food and Drugs Act, 1908."

Counsel for the Department of Health pointed out that the ordinary dose of phenolphthalein was 2 to 5 grains, whilst the amount in the tablets was 1.8 grains. The point was, he contended, that the tablets did not contain castor oil, when the label said they did. There might be an aperient of a certain nature, but this was not material to the case.

Counsel for the defence said that the tablets were purchased from a well-known manufacturer in London. The chocolates were not stated to be castor oil chocolates, but compounded castor oil chocolates, and this statement showed that there was something else present besides castor oil. Assuming each tablet to contain 2 per cent. of castor oil and 7 per cent. of phenolphthalein, castor oil would constitute 25 per cent. of the aperient agent. He contended that there was no deception of the public, as phenolphthalein was more expensive than castor oil.

The Magistrate observed that, from the point of view of the man in the street, he would think from seeing the words "Compound castor oil chocolate" that the effective chemical agent was castor oil, and for that reason the statement on the label was misleading. The defendant could have protected himself by warranty or by analysis. He found that there had been an infringement of the Act, but did not think the case was one for severe penalty. A fine of £1 and costs was imposed.

FISH MEAL WITH EXCESSIVE OIL.

ON June 4th, a feeding-stuffs merchant was charged at Newport Pagnell Petty Sessions with selling fish meal under an invoice which did not accurately set out the contents of the article sold, and contrary to the provisions of the Fertilisers and Feeding Stuffs Act, 1906.

On February 7th, 2 tons of fish meal were ordered from the defendant, who, on the same day, sent an invoice to the purchaser, which gave the following analysis of the meal: Oil, $4\frac{1}{2}$ per cent.; albuminoids, 56 per cent.; salt, under 3 per cent.

The meal was delivered on February 8th, and on February 15th, at the request of the purchaser, it was sampled by the Chief Inspector for the County.

Samples were submitted to Dr. J. A. Voelcker, the Agricultural Analyst for the County, who reported that the meal had the following composition: Oil, 11.88 per cent.; albuminoids, 50 per cent.; salt, 2.34 per cent.; and sand, 2.29 per cent. The Analyst added to his report the comment: "This is a very fluffy sample. Oil is much—and objectionably so—in excess of what is stated in the guarantee. Sand is somewhat high. Albuminoids are somewhat low, doubtless on account of the excessive oil."

This report was submitted to the Ministry of Agriculture and Fisheries, where it was decided that a prosecution should be instituted.

Dr. J. A. Voelcker, giving evidence in support of his certificate, said that the excess of oil, after making the usual statutory and other allowances, was about $6\frac{1}{2}$ per cent., an excess which was open to very strong objection on two grounds. One was the liability of the meal to upset the animal eating it. The other was a known tendency for fish oil to make bacon fat taste. Excess of fish oil had a prejudicial effect. That was so much recognised by the trade themselves that the Association of Manufacturers of Fish Meal had agreed amongst themselves to give a guarantee that their fish meal should not contain more than a certain percentage of oil. That percentage was $4\frac{1}{2}$ as a rule, or 5 per cent. If it went materially above 5 per cent. he would consider the sale to be to the prejudice of the purchaser. Albuminoids were valuable food constituents, and in this sample he found 50 per cent., instead of 56 as stated on the invoice.

Mr. James G. Stewart, Deputy Chief Inspector to the Ministry of Agriculture, and technical adviser on agriculture, stated that fish meal containing 11.88 of oil was certainly to the detriment of the purchaser on account of the liability of such a high percentage to cause taint in flesh, such as bacon; also in eggs and poultry.

Albuminoids were highly valuable in food value; therefore a deficiency of 6 per cent. was to the detriment of the purchaser, and a sample containing over 2 per cent. of sand was harmful, sand being entirely indigestible. The present sample, according to its analysis, was more suited to use for fertilising than feeding purposes.

The defendant stated that the fish meal in question was sent direct from the manufacturers. He had based his invoices on the analysis obtained from them, and he was honestly of opinion that those invoices were correct within the prescribed limits.

In cross-examination, he said that, notwithstanding a complaint he had received about a former consignment, he had not himself taken steps to have the meal analysed. The risk was the manufacturer's, not his.

Counsel for the defence submitted that the defendant was the innocent victim of circumstances, in the capacity of agent, who never saw the fish meal.

The prosecution, on the other hand, contended that the defendant had not taken any reasonable care to satisfy himself that the invoice was correct, even in the face of a complaint made to him by the same purchaser, in December, in respect of another consignment.

The Magistrates decided that reasonable care was not taken by the defendant, and they imposed a fine of £20, with £10 10s. costs.

Report of the Departmental Committee on the Fertilisers and Feeding Stuffs Act, 1906.*

IN July, 1923, a Departmental Committee was appointed by the Minister of Agriculture and Fisheries to enquire into the operation of the Fertilisers and Feeding Stuffs Act, 1906, to advise whether any, and, if so, what, amendments are necessary in order to render the execution of the Act more economical and effective, and to report accordingly.

The following members were appointed:—The Lord Clinton (Chairman), Messrs. E. R. Bolton, E. G. Haygarth Brown, C. Crowther, T. Kyle, B. S. Miller, G. Stubbs, J. F. Tocher, and J. A. Voelcker.

Evidence was received from nineteen witnesses, representing agricultural societies, merchants, manufacturers, importers, agricultural analysts, and County Councils' Associations, and this evidence is summarised in the Report.

In the introduction (Part I.) it is pointed out that many of the questions which would otherwise have needed close consideration, have already been exhaustively dealt with in the Reports of Committees set up previously.

With regard to questions of detail in connection with the specific constituents of fertilisers and feeding stuffs which would be included in a warranty, the Committee is of opinion that these would be more effectively dealt with by an *ad hoc* Committee.

A Memorandum prepared by the Ministry was circulated to all those called upon to give evidence, and it has been ascertained that, in every case, this has been accepted as a general basis on which new legislation may be founded.

In some of the recommendations the Committee has been influenced by the fact that these agreements point the way to an even balance being obtained between the conflicting views of rival interests.

* H.M. Stationery Office, Cmd. 2125. Price 1s. net.

The Report gives a historical note on the Acts of 1893 and 1906, and on the Sales for Agricultural Purposes Bill.

In Part II. it discusses the principal objections to the present Act under the following headings:—(1) The Position of the Farmer; (2) The Claims of the Merchant and Manufacturer; (3) The Case of the Importer; (4) Difficulties in Administration.

Part III. discusses proposals to remove the objections to the present Act, under the following headings:—(1) Civil Provisions; (2) Criminal Provisions; (3) Exceptional Provisions for Sales in Small Quantities; (4) Local Authorities entrusted with Enforcement of the Act; (5) Definition of the Scope of the Act; (6) Protection of the Seller against unmerited Prosecution.

Part IV. gives a summary of the principal recommendations. These would make so great a change in the existing law that they cannot be met by merely amending the Act of 1906. These recommendations are as follows:

(I) The bases of civil and criminal procedure should be clearly separated, the invoice remaining the foundation of civil claims and the description applied to the goods becoming that of criminal proceedings.

(II) The statement in the invoice should be a warranty, as at present, and no statement in the invoice should be held to relieve the seller of his civil liability.

(III) The period allowed for sampling should be extended to fourteen days after delivery of the goods or receipt of the invoice, and the requirement that notice of sampling be given to the seller should be abolished.

(IV) No sample other than those defined on page 24 as "formal" or "informal" should be analysed at the expense of the rates.

(V) The definitions in the Schedules suggested in sub-paragraph (XX) below should have effect as a warranty.

(VI) No criminal prosecution for the application of a false description should take place except in respect of a sample taken on the premises of the person to be prosecuted, or in the course of transit in a vehicle into which the consignment is loaded by him or his servants, or in the first conveyance of a public carrier into which it is loaded.

(VII) In the case of samples taken in transit, it should be necessary to provide conclusive proof that they have been taken in accordance with the Act and Regulations.

(VIII) Failure to give statutory invoice should be an offence under the Act in respect of which a prosecution may be commenced by any Local Authority administering the Act, and without the consent of the Government Department concerned. It should not be necessary to take and analyse a sample before prosecuting for this type of offence.

(IX) Every parcel of goods to which the criminal provisions of the Act apply should, when prepared for consignment or delivery, be marked in such a way as will indicate to the purchaser the name and address of the consignor and the description of the goods. It should be permissible for the name and address of the consignor to be applied by means of a mark registered with the Government Department concerned, and for the description to take the form of a code sign, of which the index must be displayed for inspection on the premises of the consignor, and a copy deposited with the Ministry or the Board. Failure to apply the description (or code sign) and the name and address of the consignor (or registered mark), or either of them, before consignment should, save in such cases as those referred to on pages 30 and 36, be an offence under the Act.

(X) A power of entry into all ports, factories, warehouses, stores and shops in which fertilisers or feeding stuffs may be manufactured or stored should be given to authorised inspectors, together with a power to take samples of goods prepared for consignment or delivery, and also a similar power of entry and taking informal samples of any article on the premises when it appears that the analysis of such article may throw light on the question whether fraudulent adulteration has, or has not, taken place on those premises. A power of entry to, and taking samples on, all farms should also be given.

(XI) Applying a false description to goods prepared for consignment should be an offence under the Act.

(XII) The presence of a deleterious substance in a feeding stuff, or the addition to a feeding stuff of a worthless ingredient the presence of which is not disclosed, should be an offence under the Act. For this purpose, Schedules to the proposed Act should be prepared to show those substances, with regard to which there may be reasonable doubt, which are to be regarded as "worthless" or "deleterious" for this purpose.

(XIII) Any discrepancy to the prejudice of the purchaser between the description attached to a parcel of goods and the invoice given in respect of it should constitute an offence under the Act.

(XIV) Where an article is described by a name comprising a name defined in the Schedules, with or without qualifying words, it should be implied that the article consists of that substance only.

(XV) Prosecutions for the offences set out in paragraphs (IX), (XI), (XII) and (XIII) should not be instituted by any Local Authority except with the consent of the central Government Department.

(XVI) No invoice should be required to be given with quantities of goods of not more than half a hundredweight sold from bulk, provided the prescribed particulars are clearly stated on a label attached to the bulk and plainly visible to the purchaser, nor with packeted goods of not more than half a hundredweight if the description appears on the package.

(XVII) The duty of administering the Act should be imposed by Statute on all County Councils and County Borough Councils in England and Wales, and all County Councils and Burgh Councils in Scotland. Power should be given to Local Authorities to establish joint Committees for the purpose of carrying out the Act, and also to exercise their powers of entry, sampling and prosecution in the area of any other Local Authority with the consent of that Authority. Concurrent powers of entry, sampling and prosecution should be vested in the Ministry of Agriculture and Fisheries and the Board of Agriculture for Scotland.

(XVIII) Local Authorities should be required to make public, at least half-yearly, the results of analyses of all formal samples, together with the name and address of the seller or consignor and the warranty given in each case.

(XIX) Inspectors under the Act should be senior wholetime officials of the Local Authority. It should be open to the Local Authorities to appoint, in addition to these Inspectors, other official Samplers for the purpose of taking samples.

(XX) The scope of the Act should be defined by Schedules which should indicate, in respect of fertilisers and feeding stuffs, (a) the name of each article or class of article to which the Act should apply; (b) the definition of the substance named; (c) the particulars to be stated in the invoice for the purpose of the civil warranty; and (d) the particulars to be stated in the description for the purpose of the criminal provisions of the Act. Provision should be made for amendment of these Schedules, and also those mentioned in paragraph (XII), by Regulations made by the Minister and the Board of Agriculture for Scotland, acting jointly.

(XXI) The defences set out in Section 2 (2) of the Merchandise Marks Act, 1887, should be provided in place of those afforded by the present Act.

(XXII) It should be provided that no civil proceedings, and no criminal proceedings in respect of the application of a false description, shall be instituted in the case of any sample unless the results of the analysis of the sample differ from the particulars stated in the invoice or in the description, as the case may be, by more than the amounts prescribed in the "limits of variation."

(XXIII) An Advisory Committee, which should subsequently become a statutory Standing Advisory Committee, should be constituted for the purpose of discharging the following functions:

1. To draw up Schedules for the purpose of prescribing:
 - (a) The fertilisers and feeding stuffs to which all the provisions of the Act should apply and those to which only the civil provisions should apply;
 - (b) Definitions of each of the articles or classes of articles to which the Act should apply;
 - (c) The statements as to the constituents present and also, possibly, as to the absence of certain substances in some instances, which should be given by the seller for the information of the farmer in the case of each article;
 - (d) Those commodities which should be regarded as "worthless" or "deleterious."
2. To recommend the terms in which the valuable constituents should be stated in the invoice (*e.g.* whether phosphates should be stated as phosphoric acid or as tri-calcium phosphate).
3. To review the limits of variation and recommend any necessary alterations or additions.
4. To consider the form of code signs and registered marks and the methods of application.
5. To review the existing Regulations and suggest such amendments and additions as may be thought desirable.
6. To recommend, from time to time, such alterations to the Schedules and Regulations as may become necessary.

In Part V. changes less fundamental in character are recommended. These refer to Sections of the Act of 1906 which, in the opinion of the Committee, contain provisions that will still be of value. The amendments suggested are as follows:

Section 1, subsections (1) and (2) appear to require re-drafting in accordance with our main recommendations.

Subsections (3), (4), (5) and (6) might usefully be incorporated, in principle, in fresh legislation.

Section 2, subsection (1) should be replaced by a provision that the Chief Agricultural Analyst shall be the Government Chemist.

Subsection (2) will require amendment, in accordance with our proposal to impose a statutory duty on all County Councils and Councils of County Boroughs to enforce the Act.

Subsection (3) seems to need no alteration.

Subsection (4) should, we think, be amended, as regards the appointment of Inspectors, in accordance with the recommendations made on page 39 of this Report.

Subsection (5). This provision should be retained and made applicable to Inspectors and Official Samplers as well as to Analysts and Deputy Analysts; but it should be provided that a person who sells agricultural produce which he has himself grown should not thereby be debarred from holding any of these appointments.

Section 3, subsections (1) to (5) and (7) require amendments consequential to our main recommendations.

Subsection (4) (b) should, further, be amended by the addition of the words "or cause to be analysed under his direction" after the word "analyse." This subsection should also be altered, in our opinion, so as to provide that a copy of the Agricultural Analyst's certificate shall be sent to the seller only where the results of the analysis differ from the warranty to the prejudice of the purchaser and by more than the amounts prescribed in the limits of variation.

Subsection (6) should, we think, be amended so as to provide for an analysis of the reserved part of a formal sample being made by the Chief Analyst, for the purpose of civil proceedings, at the request of either party and on payment of the required fee, either before or after the commencement of the proceedings.

Section 4. The proposals we have made involve wider powers to make Regulations, and the Section would, therefore, need consequential amendments.

The proviso to subsection (1) should, in accordance with paragraph (IV) of the Summary of Principal Recommendations, be deleted.

Section 5. The principal alteration we have suggested which would affect this Section is that Local Authorities should be empowered to set up Joint Committees for the purpose of carrying out the Act.

It has also been suggested that Councils should be empowered to make purchases, and we consider it necessary that this power should be specifically granted.

Section 6. The whole of this Section, with the exception of subsections (1) (a), (2) and (4), would seem to require complete redrafting.

Subsection (3) should be framed so as to permit of the analysis of the part of the sample retained by the Agricultural Analyst either by the Chief Analyst or under his direction.

Section 7 should, we think, be reproduced without alteration.

Section 8, we suggest, should remain in force and be extended by the addition of the words "or hinders, obstructs or prevents his taking such sample, or is a party to such hindrance, obstruction or prevention" after the words "purpose of analysis" at the end of paragraph (a).

Section 9 would seem to require merely drafting amendments in order to bring it into concert with the general suggestions we offer.

The provision made in subsection (2) of this Section as to the place of hearing of certain proceedings should apply to all cases of prosecution under the Act.

Section 10. We have already discussed the question of the method of stating the percentage of valuable constituents, and recommended that this matter should be dealt with by the Advisory Committee.

As regards the meaning of terms, we suggest that "delivery" should be defined so as to provide that it shall mean arrival of any consignment, whether part or whole of the purchase, at the purchaser's station, wharf or premises, or the earlier loading by him on to his own vehicle.

Ministry of Health.

REPORT ON THE COMPOSITION OF COMMONER BRITISH WINES AND CORDIALS.*

THIS report is based on a special inquiry begun in 1913, interrupted by the war, and only recently completed. It comprises information supplied by the manufacturers of British Wines and Cordials, and a classified summary of the results of the analysis of 357 samples by the Government Chemist.

SALE AND DISTRIBUTION.—Although, strictly speaking, the term “wine” should be restricted to the fermented expressed juice of any fruit, the term “British wine” has been applied to a number of beverages prepared in the British Isles, some of which contain alcohol produced, in part, by the fermentation of fresh and dried fruits, whilst others consist, for the most part, of sugar solutions flavoured with fruit juices and essences, and contain no alcohol, or only an amount not exceeding 2 per cent. of proof spirit, to which exception is not taken by the Excise Authorities. These are almost invariably described as “non-alcoholic” or “unfermented.”

The annual output of fermented wines probably does not exceed 2 million gallons per annum, but the output of temperance wines and cordials cannot be estimated even approximately.

Although wine from British-grown grapes is no longer an article of commerce, a small quantity is manufactured from imported foreign grapes by fermenting them with added saccharine matter, and a very considerable quantity is made from imported grape must.

FERMENTED BRITISH WINES.—A small amount of wine is made by fermenting the juice of various fruits, with the addition of sugar, but by far the larger proportion consists of a more or less characterless wine, made by fermenting an infusion of raisins, dried currants or rhubarb, or imported grape must, with or without added sugar, and adding distinctive essences or flavouring agents (ginger, orange peel, fruit extracts). At one time a large proportion of foreign wine was frequently added, but recent excise regulations prohibit the addition of more than 15 gallons per pipe of foreign wine to British wines

After fermentation, the wines are fined with gelatin or isinglass or by means of siliceous earths, such as Spanish clay. Colouring is effected by the addition of caramel, dried elderberries, or other vegetable colours, and, exceptionally, by aniline dyes. Of 145 alcoholic wines examined by the Government chemist, only 7 contained aniline dyes. The preservatives most commonly used are sulphurous acid and sulphites, used either in the form of burning sulphur or as bisulphite. Nearly all the samples examined contained some sulphurous acid; 14 per cent. contained it in excess of 200 mgrms. per litre; and 18·6 per cent. contained between 100 and 200 mgrms. per litre. Fourteen of 134 samples contained salicylic acid (0·25 to 1·57 grains per pint), and fluorides in small quantity were present in 8 samples. Seven samples contained boric acid in amounts ranging from 1·38 to 2·98 grains per pint. Many samples contained traces of boric acid, which has been shown to be present in the ash of genuine wine.

The proof spirit in basis wines was found to range from 14·8 to 28 per cent., and in ginger wines from 10·9 to 27 per cent. Most of the samples contained

* Reports on Public Health and Medical Subjects, No. 24, by G. C. Hancock, G.B.E., M.R.C.S., L.R.C.P., together with Report by the Government Chemist on the Examination of Samples. H.M. Stationery Office. Price 1s. 6d. net.

sugar to such an extent as to give them the character of sweet wines, and, in a few cases, "cordials."

BRITISH UNFERMENTED WINES AND CORDIALS.—These usually consist of a basis of syrup made from cane or beet sugar, supplemented, in some cases, by saccharin and, more rarely, by glucose. Of 44 non-alcoholic wines examined by the Government Chemist, saccharin was found in 10, and of 98 cordials, it was found in 7. The amount ranged from traces to 4.6 grains per pint.

The syrups are flavoured with fruit extracts, fruit essences, and artificial flavouring substances, and usually contain (1) vegetable acids, (2) colouring matters, (3) preservatives.

Of the vegetable acids, citric and tartaric acid are most commonly used. A phosphoric acid preparation called "phospho-citric acid" is sometimes used as a substitute.

Caramel and vegetable colouring matters are frequently used, and coal-tar dyes are now widely employed. Over 30 per cent. of the samples examined contained aniline dyes. These are referred to in detail in Part II. of the Report.

Preservatives.—Of 142 samples examined, 71 contained salicylic acid in amounts ranging from a trace to 11.9 grains per pint. Sulphurous acid was present in traces in nearly all the samples. In 29 cases the amount exceeded 100 mgrms. per litre. Boric acid was found in 18 samples, in amounts ranging from 1.01 to 14.31 grains per pint, and, in all but 4 cases, it was present in addition to salicylic acid or sulphurous acid.

Benzoic acid was found in 2 samples (4.7 and 10.6 grains per pint), and small quantities of fluoride were detected in 2 other samples.

As a rule, non-alcoholic wines do not contain more than 2 per cent. of proof spirit, but two samples from the same firm were found to contain 23 per cent.

Metals.—Twenty-four of the alcoholic wines and 19 of the non-alcoholic wines and cordials were examined for lead, copper and tin. None contained lead or tin, but copper was found in 22 samples in quantities ranging from 0.01 to 0.10 grain per pint. In view of this fact, the Government Chemist points out that copper has been found to occur naturally in a large number of cereals, fruits and fruit juices. (A list of references to the literature on the subject is given.) Arsenic was not found in any of the samples examined.

Tables giving the analytical details obtained with each of the samples occupy the concluding 26 pages of Part II. of the Report.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Microscopic Detection of some Fortified Milks. D. W. Horn. (*Amer. J. Pharm.*, 1924, 96, 365-366.)—The microscopic appearance of the centrifugal residues from milks is sufficiently characteristic for the ready detection of 1 part of condensed milk products in 60 of milk. The milks are centrifuged for 10 minutes at 2000 to 2100 revolutions per minute in glass tubes closed at the bottom with rubber stoppers. Smears from the residue adhering to the stoppers are air-dried and stained with methylene blue (1.25 grm. of dye in 60 c.c. of wood

alcohol.) In the case of fortified milks microscopic examination reveals numerous foreign bodies suggestive of minute starch grains. Unlike fat globules, these stain, and sometimes have the appearance of collapsed spheres. Possibly they are colloidal gel particles, as any non-reversible colloids present in the milk would, presumably, be deposited on the application of sufficient centrifugal force. The smears from fortified milks usually appear to the naked eye as lustreless and rough, with matte surfaces.

D. G. H.

"Kaschkawal." A Bulgarian Cheese. A. Heiduschka. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 47, 260-261.)—Kaschkawal, a Bulgarian cheese made from sheep's milk, or occasionally from goat's milk, is now being exported in large quantities. It appears as a pale yellow cheese similar to Gruyère and, like it, has air-spaces of 0.5 to 1 cm. diameter. The mean result of 17 analyses was as follows:—Water, 29.0; fat, 29.0; proteins, 31.3; and ash, 6.8 per cent.; refractometer number of the fat at 40° C. 41.5. Details are given of the cultural characteristics of the typical bacteria.

H. E. C.

Polarimetric Estimation of Starch in Potted Meats. A. During. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 47, 248-251.)—The following simple polarimetric method for the estimation of starch is shown to give accurate results, which also compare well with the well-known Mayrhofer method. Ten grms. of the meat are boiled on the water bath under a reflux condenser with 25 c.c. of an 8 per cent. alcoholic solution of potassium hydroxide; then 25 c.c. of hot 5 per cent. alcohol are added, and the mixture is filtered on to asbestos with the aid of the pump; in the case of very fatty foods a second treatment of the starch with alcoholic potash is desirable. The filter and the starch are mixed with a small volume of water, made neutral to phenolphthalein, after which 25 c.c. of diluted hydrochloric acid (40 c.c. of acid of sp. gr. 1.124 diluted to 1 litre) are added, and the mixture is heated in boiling water for 15 minutes; it is then cooled and made up to, say, 50 c.c. The rotation is observed at 20° C. in a 200 mm. tube. Working on 10 grms. of material and making the final volume 50 c.c., the starch is calculated from the equation:

$$\frac{\text{Observed rotation} \times 1.775 \times 2.88}{4} = \text{per cent. of pure starch;}$$

$$\times \frac{5}{4} = \text{per cent. of commercial starch.}$$

H. E. C.

New Method of Distinguishing between Honey and Artificial Honey. F. Auerbach and E. Bodländer. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 47, 233-238.)—The essential difference between genuine and artificial honey lies in the ratio of fructose to glucose; in the former this amounts to 106-119:100, and does not increase on heating or by prolonged storage. In artificial honey the ratio is less than 90:100. For the analysis the honey is warmed to about 50° C. to obtain a clear homogeneous mixture; then 2 grms. are weighed out, diluted to 250 c.c., and the total reducing sugar is estimated gravimetrically on

25 c.c. The glucose is estimated iodimetrically by adding a large excess of 0.1 *N* iodine solution, which should be about twice the iodine used, to 25 c.c. of the honey solution, together with 100 c.c. of a mixture of equal parts of 0.2 *M* sodium bicarbonate and carbonate solutions, the mixture being allowed to stand in the dark for 1½–2 hours. (Cf. ANALYST, 1923, 48, 73.) The liquid is then acidified with 12 c.c. of 25 per cent. sulphuric acid and titrated with 0.1 *N* thio-sulphate solution. A blank titration is made at the same time, with the use of similar quantities of the iodine, carbonate and bicarbonate, and sulphuric acid solutions. The difference between the two titrations represents the glucose: 1 c.c. 0.1 *N* iodine = 0.009005 gm. of glucose. The difference between the glucose and total reducing sugars is reckoned as fructose; then the above ratio is calculated.

H. E. C.

Iron Content of Spinach. A. Lichtin. (*Amer. J. Pharm.*, 1924, 96, 361–364.)—The percentage of iron in different varieties of spinach was found to vary between a maximum of 0.0087 for Long Standing and a minimum of 0.0027 for New Savoy, with an average of 0.0051 for truck spinach, 0.0568 for dehydrated spinach, and 0.00076 for canned spinach. The estimations were made by comparing the colours produced in definite concentrations of the acid extractions of the ash with standard iron solutions prepared by oxidising the ferrous salt formed from ferric ammonium sulphate and sulphuric acid with 0.1 *N* potassium permanganate solution. Most of the results are compared with those obtained by titration with potassium permanganate solution.

D. G. H.

Cacao Germ. F. Härtel. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 47, 264–266.)—Beythien and Pannwitz's observations on cacao germ (*ibid.*, 1923, 46, 230) are considered defective because they included some of the kernel; a carefully separated sample of germ gave the following analytical results: Water, 2.21; fat, 3.85; nitrogen, 5.25; sucrose, 2.98; ash, 6.76; insoluble ash, 4.46 per cent. The fat had a refractometer reading, at 40° C., of 62.5, iodine value 68.8, saponification value 169.8. The high refractometer number and high iodine value is a characteristic feature which is useful for detecting the presence of the germ in cacao products. The bye-product known as "Kakaogrus" consists mainly of ground kernels and contains a higher proportion of fat than does the germ. The fats in the kernel and shell have much lower refractometer numbers, namely, 47.6–49.1 and 50–53.5 respectively.

H. E. C.

Estimation of Dulcin by means of Xanthydrol. G. Reif. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 47, 238–248.)—In 50 per cent. acetic acid solution at ordinary temperatures dulcin combines quantitatively with xanthydrol, forming exactly twice its weight of xanthyl-dulcin, which is a colourless crystalline substance of m.p. 246° C., and is readily soluble in water, alcohol, ether and similar solvents. This reaction is useful for the estimation of quite small quantities of dulcin. As saccharin and certain other substances are liable to interfere, they are eliminated by lead acetate precipitation and subsequent extraction of the dulcin with ethyl

acetate in alkaline solution. The method, as applied to a fruit syrup, is as follows:—Fifty grms. of the syrup, diluted with 60 c.c. of water, are acidified with 20 drops of acetic acid, 10 c.c. of a 20 per cent. solution of lead acetate solution are added, and the mixture is allowed to stand for an hour. Then, after ascertaining that excess of lead has been added, the precipitate is filtered off, and the lead removed from the filtrate by the addition of 20 c.c. of a saturated solution containing 20 grms. of sodium sulphate and sodium phosphate in 100 c.c. After allowing the mixture to stand for a few hours it is filtered, and the filtrate made just alkaline and then shaken out twice with an equal volume of ethyl acetate, which is the best solvent for extracting dulcin. The mixed ethyl acetate extract is distilled on a water bath, and the residue is dissolved in 15 c.c. of boiling water and filtered; then the aqueous solution is evaporated to dryness on the water bath, and the residue of crude dulcin is dissolved in 20 c.c. of 50 per cent. acetic acid, the solution filtered, and the filter washed with a further 20 c.c. of the 50 per cent. acid. To this solution is added 0.2 gm. of xanthinol dissolved in 3 c.c. of hot methyl alcohol; after standing for about 2 hours the precipitate is filtered off on to a Gooch crucible, washed with a small quantity of the acetic acid, dried at 100° C., and weighed.

H. E. C.

Ethylene Glycol. Its Properties and Uses. H. C. Fuller. (*Ind. Eng. Chem.*, 1924, 16, 624–626.)—Ethylene glycol, $C_2H_4(OH)_2$, sp. gr. 1.116, is a colourless, odourless liquid having a sweetish taste; it is miscible with water in all proportions and bears a considerable resemblance to glycerol, although less viscous than this substance. It appears to have some use as a solvent, particularly in the preparation of flavouring extracts and pharmaceutical products, in which it may replace alcohol. As a preservative ethylene glycol is about equal to alcohol, and is much superior to glycerol; when taken in moderate doses it has no injurious physiological action.

W. P. S.

Analysis of Pharmaceutical and Bacteriological Gelatins. E. Cattelain. (*J. Pharm. Chim.*, 1924, 29, 444–447.)—Certain modifications of the French Pharmacopoeia requirements are suggested. Since all the samples examined were found to be acid and not neutral, the *acidity* should be determined by dissolving the dehydrated product in water and titrating the solution at 50° C. with *N* sodium hydroxide solution, with phenolphthalein as indicator. The acidity, expressed as hydrochloric acid, should not exceed 1.5 per cent. Gelatin ash constantly contains iron, and the prescribed reaction with hydrogen sulphide is therefore always positive and does not allow of the recognition of other metals, particularly of copper. *Iron* should be estimated by moistening 1 gm. of ash with nitric acid, evaporating to dryness, heating to a dull red heat, adding 10 c.c. of 10 per cent. hydrochloric acid, and heating on a water bath until nearly dissolved. Evaporation is then carried to dryness, the residue treated with 20 c.c. of 5 per cent. hydrochloric acid, and the insoluble matter filtered off. Ammonium hydroxide is added to the filtrate until the precipitate is permanent, and, subsequently, acetic acid. The insoluble ferric phosphate is washed with distilled water until the

filtrate gives no precipitate with ammonium oxalate, calcined and weighed, and the result multiplied by 52.98 to give the percentage of Fe_2O_3 in the ash. This should not exceed 2 per cent. *Copper*. The filtrate should not be coloured by the addition of 1 or 2 drops of 1 per cent. ferrocyanide solution. *Manganese* is nearly always present. Its amount should not be sufficient, on application of the Marshall-Bertrand process of dissolving 0.1 grm. of the ash in 10 c.c. of 0.25 nitric acid, adding 5 drops of 10 per cent. silver nitrate solution and 0.25 grm. of powdered potassium persulphate, and boiling, to produce a rose or violet coloration. The ash of the gelatin should not exceed 1.5 per cent. D. G. H.

Biochemical, Bacteriological, etc.

Preparation and Estimation of Methæmoglobin. M. Nicloux and G. Fontès. (*Comptes rend.*, 1924, 178, 1757-1759.)—Treatment of blood with one-tenth of its volume of 95 per cent. alcohol constitutes a simple method of preparing methæmoglobin from the oxyhæmoglobin, the change occupying about six weeks at the ordinary temperature, or about a week at 37° C. The fact that alcohol prevents putrescence of blood and, hence, the conversion of methæmoglobin into hæmoglobin by the reducing processes accompanying putrescence renders it possible to manipulate methæmoglobin solutions in a medium closely comparable with blood and to estimate the pigment.

When blood (10 to 20 c.c.) containing a mixture of methæmoglobin and oxyhæmoglobin is shaken for an hour with pure carbon monoxide, the amount of the gas fixed is proportional to the amount of oxyhæmoglobin (*a*) present, since the other pigment does not combine with carbon monoxide. The gas dissolved physically is then removed in a vacuum, and the combined carbon monoxide extracted and estimated eudiometrically. The residual blood is treated with sodium hydrosulphite in dilute ammoniacal solution, both the oxyhæmoglobin and the methæmoglobin being thus converted entirely into hæmoglobin. The total hæmoglobin is then combined with carbon monoxide, as before, and its amount (*b*) estimated. The percentage of oxyhæmoglobin in the mixed pigments of the blood is given by $100 a/b$, and that of methæmoglobin by $100 (b-a)/b$.

T. H. P.

Chemistry of the Pyrimidines. O. Baudisch. (*J. Biol. Chem.*, 1924, 60, 155-166.)—At one time it seemed as if the pyrimidines, uracil and cytosine, behaved entirely differently. On treatment, however, with ferrous bicarbonate and air and subsequent autoxidation of the colourless intermediate products, they formed the same brilliant lemon-yellow pigment possessing special chemical properties. This pigment-formation by such mild treatment is remarkable biologically, and also physically, since by the change the absorption of light is extended far into the visible spectrum. The yellow pigment is formed more quickly from cytosine than from uracil, due to the catalysing action of the ammonia produced in the cytosine experiment. In alkaline solution at 37° C., the pigment is weakly autoxidisable itself, since the yellow colour gradually disappears from

the surface. It may also be obtained from a synthetic isobarbituric acid. It has not been analysed, but possibly there is a linking of two carbon atoms, 5 of the pyrimidine ring, forming a bimolecular pinacone-like compound. The pigment, characterised by a great stability toward both acids and alkalis, shows different chemical reactions according to whether one deals with weakly acid or weakly basic solution. In basic solution it reduces phosphomolybdic acid with the formation of an indigo blue colour and reduces ammoniacal silver nitrate solution slowly in the cold and quickly on heating. With diazobenzenesulphonic acid it gives an intense, but temporary, brilliant red colour. Methylene blue solutions are decolorised quickly, but an intense blue colour appears at the surface, due to the absorption of oxygen from the air. This reaction shows the reduction and oxidation power of the pigment in alkaline solutions. In acid solution the yellow pigment is very susceptible to reducing agents. Zinc dust easily decolorises it, but, on warming the colourless solution in an open bath, the yellow colour returns on autoxidation. The biochemical significance of the pigment is discussed, and details of the experimental work are given. It is assumed that the pyrimidines, uracil and cytosine, or their decomposition products, dihydroisobarbituric acid (not yet isolated), isobarbituric acid and the brilliant yellow compound possess the functions of respiration pigments. A deeper insight is obtained into the necessity of iron which is found in every cell nucleus. The system—ferrous bicarbonate plus air—causes the addition of one molecule of water to the ethylene group in uracil and in cytosine, giving dihydroisobarbituric acid. P. H. P.

Titration of Chlorides in Plant Fluids. J. V. Lawrence and J. A. Harris. (*J. Amer. Chem. Soc.*, 1924, **46**, 1471–1477.)—The results of tests of a wet oxidation and modified Volhard method for the rapid and accurate estimation of chlorides in plant tissue fluids are given. All the chlorides are precipitated by the addition of known excess of silver nitrate solution. Organic substances that introduce a source of error by fixing some of the silver added to the fluids, and pigments which preclude the detection of end-points in titration may be effectively and conveniently eliminated as sources of error by boiling with concentrated nitric acid. When silver chloride is thus precipitated from solution it is agglomerated into masses, as noted by Whitehorn (*J. Biol. Chem.*, 1921, **45**, 449), and titration of the excess of silver nitrate, with a standard solution of potassium thiocyanate, may be carried out in the presence of the precipitated silver chloride. Iron alum is used as an indicator. The solutions required and the analytical procedure are given and the accuracy of the method is discussed. Many hundreds of analyses have been made on a wide range of plant materials during the past three years. The method developed and used extensively for plant tissue fluids gives excellent results for blood chlorides, but is not recommended for this purpose because of the resistance of the hæmoglobin to the action of nitric acid, although, since this was written, Van Slyke (*J. Biol. Chem.*, 1923, **58**, 523) has suggested essentially the same method for blood. That it is applicable to fluids of much higher protein content than that found in plant saps is shown by the fact that it has already been used in the analysis of hides. P. H. P.

Toxicological and Forensic.

Solubility of Arsenic in Beverages. S. Goy and E. Wende. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 47, 267-269.)—The amount of arsenic dissolved when solid arsenious oxide is added to liquid food depends upon the variety of arsenious acid used, as well as on the time and temperature, but is always much less than the recorded solubility figures for water. The following amounts of arsenious oxide per 100 c.c. were found in solution when the finely powdered amorphous substance was shaken with liquids for 3 minutes and filtered:

Coffee, 2 per cent. infusion, temp. 72 C.	0.041	gram.
Coffee substitute,	0.04	..
Tea, 0.5 per cent. infusion	0.04	..
Tap water	0.26	..
Seltzer water, cold	0.013	..
Tap water	0.016	..
Beer	0.011	..

H. E. C.

Outbreak of Poisoning due to Cayenne Pepper containing Lead. M. Nicoloff. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 47, 269-270.)—Adulteration of cayenne pepper is rife in Bulgaria, where much is used for seasoning food; the addition of maize-meal, sawdust and bran, with a dye, has been common, and, during a recent shortage, sunflower chips (that is, sunflower seeds after extraction of the oil) have been extensively used. In 1923 more than 1000 persons were affected by an outbreak of lead poisoning which was traced to adulteration of cayenne with 20 per cent. of red lead.

H. E. C.

Potatoes containing a large amount of Solanine. E. Schowalter and W. Hartmann. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 47, 251-257.)—Arising out of an outbreak of potato-poisoning in 1922 it is noted that the commonest physiological effect of solanine is to produce a constriction of the throat and sickness; it is also observed that partial immunity may be acquired. Experiments were made to find whether or not the use of potatoes with a high solanine content gives rise to a crop containing an excessive quantity when used for seed purposes, and these show that such seeds produce quite a normal content in the crop. There is no apparent connection between the type of soil or system of manuring and the solanine content; the high amount may have been due, in the year 1922, to the abnormal rainfall in the areas concerned. The increase in solanine content on storage is more than can be accounted for simply by loss of water, and appears to take place mainly in the outer layers of the potato, although it is not dependent upon the access of light. (*Cf. also Bömer and Mattis, ANALYST, 1924, 284.*)

H. E. C.

Total Reduction of Nitrates and Chlorates during Putrefaction of Viscera. C. Ghigliotto. (*Ann. Chim. anal.*, 1924, 6, 161.)—The viscera of two persons who had died after eating food which had been seasoned with sodium nitrate in error for sodium chloride were analysed six days after death when in a very advanced state of decomposition. They were tested for nitrate by Ogier's diphenylamine test, with a negative result. To establish whether or not nitrates could be entirely reduced during putrefaction, two flasks of nutrient broth were prepared similar to the suspected food and containing wheat-flour and beans, together with several drops of intestinal juice. To one flask were added 2 grms. of sodium nitrate per 700 c.c. of the broth, and to the other 10 grms. On testing both gave at once a positive result with diphenylamine. They were incubated at 37° C., and tested for nitrate at intervals. The flask containing 2 grms. gave a negative result at the end of 4 days; that containing 10 grms., after 11 days.

A similar experiment was made with potassium chlorate, and it was found that whereas with nitrate a very foetid odour was evolved, there was no disagreeable smell formed when chlorate was used (0.5 to 1 gm.), and a small white pellicle formed. When 0.5 gm. of potassium chlorate per 700 c.c. of broth was used the diphenylamine reaction was negative on the fourteenth day; with 2.5 grms. the result was negative on the twentieth day.

R. F. I.

Water Analysis.

Estimation of Manganese in Water by the Sodium Bismuthate Method.

W. D. Collins and M. D. Foster. (*Ind. Eng. Chem.*, 1924, 16, 586.)—The following procedure is recommended for the estimation of manganese by the bismuthate method. A quantity of the water (100 c.c.) containing not more than 1 mgrm. of manganese is treated with 10 c.c. of dilute nitric acid (1:3) and 1 c.c. of concentrated sulphuric acid, evaporated, and the residual solution heated until most of the sulphuric acid has been expelled. The residue is dissolved in 50 c.c. of water and 20 c.c. of dilute nitric acid (through which air has been bubbled to remove lower nitrogen oxides), 0.1 gm. of sodium bismuthate is added, and the mixture is stirred for one minute and filtered through an alundum crucible or through an asbestos filter which has been washed with permanganate solution. The filtrate is diluted to a definite volume and its colour compared with standards. These are prepared by measuring out definite volumes of standard permanganate solution, adding to each the same quantity of nitric acid as that used for the sample, and diluting the mixtures to the same volume.

W. P. S.

Organic Analysis.

Dehydration of Alcohol by means of Glycerin. E. Knecht and E. F. Muller. (*J. Soc. Chem. Ind.*, 1924, 43, 177-178T.)—Distillation at a temperature not exceeding 80° C. of alcohol to which glycerin has been added in the proportion of 25 per cent. by weight of glycerin for 10 per cent. of water present,

(20 per cent. for 5 per cent. of water, or 15 per cent. for 2 per cent. of water) followed by a second distillation with the use of smaller quantities of glycerin, was found to remove almost the whole of the water present. Rectification may be carried out in one operation, either by causing the distilled vapour, before reaching the condenser, to pass through 3 narrow wash bottles containing glycerin and heated to 78° C., or through an inverted upright condenser heated by a current of steam through the jacket and filled with glass beads over which glycerin trickles at the rate of 1 drop in 5 seconds. A 99.5 per cent. product is easily obtained at an additional cost of 4d. to 5d. per lb., and the process has the advantage of speed. The authors draw attention to the somewhat similar method recently proposed by Mariller for commercial dehydration of alcohol. (*Chim. et Industrie*, 1923, Oct.)

D. G. H.

Oxidation of Acetic Acid by different Metallic Chromates. L. J. Simon. (*Comptes rend.*, 1924, 178, 1816-1819.)—Under the conditions employed in the author's method of estimating carbon in organic compounds (*cf.* ANALYST, 1922, 47, 405; 1923, 48, 37, 398), low results, and also an increased proportion of carbon monoxide, are obtained with acetic acid if the silver dichromate is replaced by an equivalent amount of another dichromate.

T. H. P.

Estimation of Acetic and Butyric Acids. E. Fylemann (*J. Soc. Chem. Ind.*, 1924, 43, 142-143 T.)—In fermented liquids butyric acid may be estimated with considerable accuracy by boiling the liquid with excess of potassium dichromate in a sulphuric acid solution of definite strength, the butyric acid being thus oxidised to acetic acid and carbon dioxide, and the dichromate being reduced to the extent of the equivalent of six atoms of oxygen. Propionic acid exerts a reducing action equivalent to three atoms of oxygen, and an allowance must be made for acetic acid, although this is almost unattacked.

The distillate containing the volatile acids is titrated as usual with 0.25 N sodium hydroxide solution (*n* c.c. required) in presence of a minimum quantity (2 drops) of ordinary alcoholic phenolphthalein, and is then boiled to one-half of its volume in order to eliminate the alcohol and afterwards diluted until 20 c.c. of the liquid correspond with about 1 c.c. of 0.25 N sodium hydroxide. Twenty-five c.c. of 0.25 N potassium dichromate are added to 20 c.c. of the liquid in a 300 c.c. conical flask, to which is fitted a reflux condenser; 30 c.c. of 96 per cent. sulphuric acid are then introduced by way of the condenser, the flask being shaken meanwhile. The liquid is at once boiled for exactly an hour, and then cooled, diluted to about 250 c.c., mixed with potassium iodide, and titrated with 0.25 N thiosulphate solution.

Apart from the correction for acetic acid, 1 c.c. of 0.25 N dichromate solution, which is equivalent to 8 grms. of available oxygen per litre, represents $80 \div (6 \times 8000) = 0.00183$ grm. of butyric acid. Should propionic acid be present, this cannot be distinguished from butyric acid by this method, but as the oxygen absorbed is proportional to the increased weight of organic acids, the total weight of organic acids is correctly determined. Since the oxidation to acetic acid occurs mostly in a

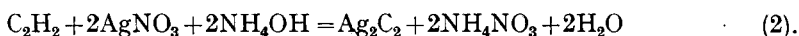
very few minutes, the correction for this acid may be based on the organic acid originally present, that is, on the total acidity, and is equal to $0.5 n$. Thus, if b c.c. of dichromate are reduced, $0.00183 (b - 0.5 n)$ grms. of butyric acid are present in the amount of distillate employed. In the case of propionic acid, the amount is $74 (b - 0.5 n) \div (3 \times 8000) = 0.00308 (b - 0.5 n)$.

T. H. P.

Estimation of Calcium Carbide. J. Y. Yee and H. J. Krase. (*J. Amer. Chem. Soc.*, 1924, **46**, 1389-1393.)—An accurate method has been developed for the estimation of carbides that yield acetylene when treated with water, by the application of the method of Chavastelon, as modified by Ross and Trumbull (*J. Amer. Chem. Soc.*, 1919, **41**, 1180) for the analysis of gas mixtures containing acetylene and ethylene. Chavastelon's method involves the absorption of acetylene in neutral or ammoniacal silver nitrate. With the neutral solution and an excess of silver nitrate the reaction is quantitative according to the equation



It is also quantitative with ammoniacal silver nitrate,



In the first reaction the liberated nitric acid can be directly titrated, and in the second the excess of silver nitrate must be found. Both methods are satisfactory for carbides, the former being the more rapid of the two, but for carbides containing nitrides reaction (2) must be employed. Full experimental details are given; also precautions necessary and a diagram of the apparatus required. Traces of sulphides do not interfere when proper precautions are taken. Phosphides, however, should be absent. Some results given shew that the two methods agree satisfactorily.

P. H. P.

The Sodium Plumbite Test of Gasoline. B. T. Brooks. (*Ind. Eng. Chem.*, 1924, **16**, 588.)—In this test the gasoline (light petroleum) is shaken with litharge dissolved in sodium hydroxide solution; if the sample contains sulphur compounds a yellow coloration develops. A very small quantity of sulphur is then added and the mixture again shaken, when the colour is much intensified, a flocculent precipitate forms, and the colour changes rapidly from dull orange to brown and finally brownish-black. Although practically all the gasoline refined to-day is free from sulphur compounds and does not give a coloration with the test, certain specimens which have been kept for a few months yield a coloration and a brownish precipitate; this is due to the formation of organic peroxides in the gasoline, and the precipitate consists of lead peroxide. In these cases, the addition of sulphur does not intensify the colour. If allowed to stand for a few hours, the precipitate due to sulphur compounds becomes quite black, whilst the lead peroxide precipitate retains its brownish shade.

W. P. S.

New Form of Fenchone Oxime. Characterisation of Fenchone in presence of Camphor. M. Delépine. (*Comptes rend.*, 1924, **178**, 1721-1723.)—Fenchone in presence of camphor may be readily detected by converting the mixed compounds into their oximes and taking advantage of the greater solubility and

more marked acidic character of camphor oxime. A solution of a mixture of equal amounts of the two oximes in 5 to 7 times their weight of boiling alcohol deposits one-half of the fenchone oxime in crystals having $[\alpha]_D = +45^\circ$, fresh crystals with $[\alpha]_D = +47^\circ$ being obtained on addition of potassium hydroxide and water to the mother liquor; acidification of the alkaline liquid by means of acetic acid then yields camphor oxime with $[\alpha]_D = -40^\circ$. Two new fenchone oximes (β) have been prepared, one dextro-rotatory and one lævo-rotatory. There are thus six fenchone oximes known, the α - and β -oximes existing in dextro-, lævo-, and racemic modifications.

T. H. P.

New Reaction for Low Temperature Tars. **F. Schulz and J. Prunet.** (*Bull. Soc. Chim.*, 1924, 35, 638-641.)—When 1 to 2 c.c. of a lignite tar, or any of the oils obtained therefrom by distillation, are shaken for about a minute with 5 c.c. of a solution containing 25 grms. of crystallised potassium oxalate per 100 grms. of solution and treated just before use with a few drops of ferric chloride solution, the lower layer which separates on standing assumes an indigo coloration. This reaction, which is due largely to the catechol present in the tar or tar oil, is not shown by aromatic coke-oven or gasworks tars or their distillates, but is given by tar obtained by distilling certain coals at low temperatures in glass retorts, the substances determining the reaction apparently undergoing destruction at a high temperature.

T. H. P.

Estimation of Glycerol by Oxidation with Iodate and Sulphuric Acid. **R. Strebinger and J. Streit.** (*Zeitsch. anal. Chem.*, 1924, 64, 136-143.)—Potassium iodate and strong sulphuric acid oxidise glycerol quantitatively, and the excess of iodate can be estimated iodimetrically. The percentage of glycerol is given by the expression $\frac{92 \cdot 1 (a - b) 100}{599 \cdot 26 E}$, in which a = iodate added b = remaining iodate, and E = weight of substance taken. About 0.2 to 0.3 (or, with dilute solutions a quantity containing 0.025 to 0.05) grm. of glycerol, 8 to 9 times its weight of potassium iodate (accurately weighed), and 30 c.c. of pure, strong sulphuric acid are heated in a conical 300 c.c. flask on a sand-bath; in the case of dilute solutions the quantity of sulphuric acid must be increased to 50 c.c. Copious evolution of iodine vapour sets in at 170°C . The temperature is gradually raised until the iodine is expelled and white fumes appear. The acid retains a little iodine, which colours it green. When cold, it is diluted with water, when the colour changes to brown. The liquid is boiled till colourless, again diluted and made up to volume in a graduated 250 c.c. flask. Fifty c.c. are titrated, after addition of 1 to 2 grms. of potassium iodide, with 0.1 *N* thiosulphate solution standardised against potassium iodate. For the estimation of glycerol in fats, 2 to 3 grms. are saponified with 5 grms. of caustic alkali in 30 c.c. of water and 10 c.c. of methyl alcohol for 2 to 3 hours under reflux. The alcohol is expelled on the water-bath, and the hot liquid treated with dilute sulphuric acid, and cooled. The fatty acids are filtered off on a wet double paper, and well washed, and the

filtrate evaporated to one-half its bulk on the water-bath. If this causes a precipitate of albuminous matter (as in the case of tallow), the liquid is again filtered through a wet paper, which is subsequently well washed. The filtrate is ready for the estimation of the glycerol.

W. R. S.

Tung Oil. Oil from the Seeds of *Aleurites montana*. R. N. Parker, M. G. Rau, W. A. Robertson, and J. L. Simonsen. (*Indian Forest Rec.*, 1924, 10, 1-13.)—Some confusion exists in the literature of the subject as to the species of *Aleurites* from which Chinese wood oil is obtained; Hankow wood oil is derived from the seeds of *A. Fordii* and that from Canton from *A. montana*; the botanical characters of these seeds and leaves are described and illustrated. The oil from Southern Japan, which is derived from *A. cordata*, is not exported to Europe. Examination of the oil from *A. montana* shows it to consist of the glycerides of β -elaeostearic, oleic, and probably linolic acids, whereas Fahrion has shown that the oil from *A. Fordii* consists of glycerides of α -elaeostearic and oleic acids. The following table gives the data obtained in the analysis of oil from these species, and a comparison with the proposed American standard.

	<i>A. montana</i> .	<i>A. Fordii</i> .	American specification.
Specific gravity at 15°/15° C.	0.9467	0.9439	0.939-0.943
Refractive index, n_D^{15}	1.494	1.4917	n_D^{25} 1.515-1.520
Acid value	3.4	nil	7.0 max.
Saponification value	203	204	190-195
Unsaponifiable matter, per cent.	0.6	—	0.75
Iodine value	141.4	157.7	163
Heat test	16'	12.5'	12'
Iodine jelly test	45"	35"	—
"Titre test"	54-54.5°	—	—

The heat test is considered the most satisfactory criterion.

H. E. C.

Phytosterols of the Endosperm of Maize. R. J. Anderson. (*J. Amer. Chem. Soc.*, 1924, 46, 1450-1460.)—The unsaponifiable matter derived from the endosperm of maize contains at least two fractions of phytosterol that differ in properties and composition. The endosperm of maize contains some free phytosterol; m.p., 137-137.5° C.; specific rotation -32.23°; acetyl derivative, m.p., 127° C. After saponification, the unsaponifiable matter was separated into the following 3 parts: (1) The optically active dihydrositosterol, $C_{27}H_{47}OH.H_2O$; m.p., 138-139° C. The dried preparation melts between 140 and 141° C.; $[\alpha]_D^{20}$, +25°; acetyl derivative, m.p. about 138° C.; $[\alpha]_D^{20}$, +14.41°. (2) Rather large quantities of the ordinary sitosterol associated with the dihydrositosterol in the endosperm and bran of maize. (3) A brownish-yellow oily substance that has not been examined. Dihydrositosterol crystallises in the same form as sitosterol, but the crystals are larger and denser. It does not give the Liebermann-Burchard reaction, and the Whitby reactions are not typical. It does not absorb bromine. All the experimental work is described in detail, and results of combustions are given. The laevorotatory sitosterol and the dextrorotatory dihydrositosterol exist in

various plant fats. The author finds that the magnitude of the optical rotation is a safer and more reliable criterion of purity in these compounds than is the melting point. Plants may elaborate several different phytosterols, and these may be deposited in special parts of the plants. P. H. P.

Substitutes for Mercuric Chloride in Hubl's Iodine Solution. B. M. Margosches and W. Hinner. (*Chem. Zeit.*, 1924, 48, 389-391.)—The influence of mercuric chloride and the various substitutes which have been proposed for it in connection with the estimation of the iodine value of oils has been experimentally studied. The activation of an alcoholic iodine solution by mercuric chloride depends on the formation of mercuric iodide and iodine monochloride, and a similar effect is produced by cadmium chloride; the mercury, as such, has no specific action. In the case of Ley's solution of iodine and mercuric acetate in acetic acid there is similarly the production of mercuric iodide and acetic acid from the hydriodic acid formed from the fat. In the solution of iodine and mercuric iodide in methyl alcohol, proposed by Gill and Adams, there is formed an even greater quantity of acid than with Hubl's solution; the accelerating effect of the mercuric iodide is mainly due to its combination with the hydrogen iodide formed during the reaction, which would otherwise retard it. H. E. C.

Bromometric Estimation of Iodine Values. W. Manchot and F. Oberhauser. (*Zeitsch. Unters. Nahr. Genussm.*, 1924, 47, 261-263.)—The authors confirm the reliability of Rosenmund and Kuhnenn's method, in which the reagent is pyridine sulphate bromide, $C_6H_5N.H_2SO_4.Br_2$ (*cf. ANALYST*, 1924, 105), and show that a 0.1 N solution of bromine in 20 per cent. hydrochloric acid also gives accurate results when using chloroform as solvent and allowing a time of 4 hours. Similar results are obtainable in 12 hours in the absence of chloroform. As an alternative, bromine in technical (99 per cent.) acetic acid is satisfactory. A mixture containing 0.2 per cent. of indigo carmine and 0.2 per cent. of trinitroresorcinol is a more satisfactory indicator than is methyl orange in the final titration, which is carried out as described by Rosenmund and Kuhnenn. H. E. C.

Nitrosomethylurethane as a Reagent for Catechol Tans. W. Vogel and C. Schüller. (*Coll.*, 1923, 642, 319.)—Ten to twelve c.c. of clear filtered tannin solution of analytical strength are treated in a test-tube with 3 to 5 drops of 10 per cent. hydrochloric acid. The solution should remain clear on boiling. To the boiling solution are added 5 to 7 drops of nitrosomethylurethane, and the boiling continued for 3 to 4 minutes. The solution must be allowed to cool slowly, when, if catechol tans are present, a precipitate is formed. The precipitation is, in general, characteristic for catechol tans. Pyrogallol tans give no precipitate. The above reaction is five times as sensitive as the bromine-water test, and possesses the further advantage that it is not influenced by the presence of sulphited tans, synthetic tans or cellulose extracts. R. F. I.

Microchemical Tests for Hexamethylenetetramine. H. Leffmann. (*Amer. J. Pharm.*, 1924, 96, 366-367.)—A small fragment of the sample is dissolved

in a drop of water; a drop of concentrated hydrochloric acid and 2 drops of a magenta and sulphurous acid solution are then added. If hexamethylenetetramine is present a bluish tint develops, gradually deepening in intensity. This test is suggested as more convenient than, and as delicate as Denigès' method (*Bull. Pharm. Bordeaux*, 1924, **62**, 3) which consists in the microscopical examination of the residue from the solution of the fragment of sample in 1 volume of alcohol and 2 volumes of chloroform, and subsequent recrystallisation with various reagents.

D. G. H.

Inorganic Analysis.

Separation of Mercury from Cadmium by means of Pyridine. G. Rotter. (*Zeitsch. anal. Chem.*, 1924, **64**, 102-106.)—The neutral solution is treated with excess of ammonium thiocyanate, warmed gently, and treated, after cooling, with one-third of its volume of pyridine. After standing for at least one hour the heavy white crystalline precipitate of cadmium pyridine thiocyanate— $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_2](\text{CNS})_2$ —is filtered off and washed on a paper previously moistened with a solution of thiocyanate and pyridine. Re-precipitation is recommended. The precipitate is dissolved in a minimum of hydrochloric acid (1:10); the solution is neutralised with ammonia, and again treated with thiocyanate and pyridine. After standing as before the precipitate is filtered off, washed with the above washing-solution, dissolved in nitric acid, the solution evaporated to dryness in a tared crucible, and the residue ignited. After treating with sulphuric acid, the cadmium sulphate is weighed. Mercury is precipitated in the combined filtrates as sulphide.

W. R. S.

Separation of Cadmium from Zinc. K. Chalupny and K. Breisch. (*Chem. Zeit.*, 1924, **48**, 349-351.)—The solution is neutralised with potassium hydroxide until a slight permanent precipitate is obtained; this is dissolved by addition of potassium cyanide solution (100 grms. in 300 c.c. water), followed by an excess of the same solution equivalent to 4 grms. of salt per gm. of zinc. The clear liquid is made alkaline with 10 c.c. of 4 N potassium hydroxide, and heated; at the boiling point 0.5 to 1 gm. of solid thio-urea is added, and boiling is continued for 30 minutes after the appearance of the precipitate of cadmium sulphide. This is filtered off at once and washed several times with hot dilute cyanide, and then with hot ammonium nitrate solution. The washed precipitate is dissolved in hot dilute hydrochloric acid, and the precipitation repeated in exactly the same manner. The authors estimate the cadmium by electrolysis; the sulphide is dissolved as before and the hydrogen sulphide boiled off; the solution is treated with potassium hydroxide until the appearance of a slight permanent precipitate. This is dissolved in a very small excess of cyanide, and the solution is electrolysed at 80° C. (5V, 5 Amp.), 0.05 gm. of metal being deposited in 30 to 45 minutes. The results are accurate. For the estimation of cadmium in spelter, the solution of a suitable quantity of metal is digested with 0.5 gm. of purest zinc filings at 80° C. for 2 hours. The precipitate is filtered off, dissolved in hydrochloric acid, and the cadmium estimated as described.

W. R. S.

Use of the Lead Cathode in the Electrolytic Method for the Estimation of Minute Quantities of Arsenic. T. Callan. (*J. Soc. Chem. Ind.*, 1924, 43, 168-170T.)—A series of experiments was carried out with a view to elucidating the erratic behaviour of lead cathodes continuously used in the electrolytic estimation of arsenic. The two main ways in which such cathodes may lose their sensitiveness were found to be: (1) By prolonged use in dilute sulphuric acid solutions, possibly due to a coating of a film of lead sulphate or oxysulphate. Inactivity in such cases is removed by treatment with dilute nitric acid, and it is strongly recommended that before every test lead cathodes be dipped for a few minutes in dilute nitric acid (with immediate removal on evolution of gas) and well washed. (2) By removal of traces of metallic impurity from the surface; this may be remedied by the addition of a trace of cadmium to the cell immediately before the addition of the solution to be tested. (*Cf. ANALYST*, 1922, 47, 535.)

D. G. H.

Detection and Estimation of Antimony by means of Pyrogallol. F. Feigl. (*Zeitsch. anal. Chem.*, 1924, 64, 41-47.)—Pyrogallol yields with antimonious salts a white, silky, crystalline precipitate of the composition $\text{SbC}_6\text{H}_5\text{O}_4$ (Sb 46.01 per cent.). The reaction takes place quickly and quantitatively in moderately acid solution; tartrate solutions are most suitable. The sensitiveness of the reaction is 1 in 217,400. For quantitative estimations the solution of antimony trichloride is treated with an equivalent amount of Rochelle salt and about five times the necessary amount of pyrogallol dissolved in 100 c.c. of water. The volume is made up to 250 c.c., the precipitate collected, after 2 hours' standing, on a Gooch crucible, washed with cold water, dried, and weighed. The process allows of a separation from arsenic, which is not precipitated, and may be recovered from the filtrate as sulphide.

W. R. S.

Volumetric Estimation of Tin. J. G. F. Druce. (*Chem. News*, 1924, 128, 273.)—The method of Knop for the titration of ferrous iron with dichromate, with diphenylamine as indicator (*J. Amer. Chem. Soc.*, 1924, 46, 263), was extended to the estimation of stannous salt. The solution was treated with excess of ferric salt, and the ferrous salt formed titrated with 0.1 N dichromate solution; a drop of a solution of one grm. of diphenylamine in 100 c.c. of strong sulphuric acid served as indicator. Fifteen c.c. of acid mixture (equal volumes of strong sulphuric and phosphoric acids) were added where large amounts of dichromate were required, the end-point being marked by the appearance of a blue coloration. It was found feasible to titrate stannous salt in the manner described, without previous addition of ferric salt. According to the results given, the new method gives substantially higher results than the iodine method.

W. R. S.

Precipitation of Platinum and Copper as Sulphides. R. Doht. (*Zeitsch. anal. Chem.*, 1924, 64, 37-40.)—The gently boiling platinum solution, free from nitric acid, and containing 5 c.c. of hydrochloric acid, is treated with a 10 per cent. solution of sodium hypophosphite, then, while being constantly stirred, with an

aqueous solution of sulphur dioxide. The platinum is precipitated as sulphide, which is allowed to settle on the water-bath, filtered, washed with hydrogen sulphide water containing ammonium nitrate, and ignited strongly to metal. Copper solutions, when treated in the same manner, also yield a precipitate of sulphide. It is assumed that the sulphur dioxide is first converted into hyposulphurous acid, which is reduced further as follows: $\text{H}_2\text{S}_2\text{O}_4 + 2\text{H}_3\text{PO}_2 = 2\text{H}_3\text{PO}_4 + \text{H}_2\text{S} + \text{S}$.

W. R. S.

Separation of Zinc by Electrolytic Deposition from Alkaline Solutions

K. Breisch. (*Zeitsch. anal. Chem.*, 1924, 64, 13-23.)—Nitrates interfere with the electrolysis of zinc in alkaline solution, as deposition does not begin until they have been completely reduced to ammonia. It was found that the nitrates can be eliminated as follows: The solution (150 c.c.) is heated to boiling with 50 c.c. of strong hydrochloric acid, and treated with small quantities of solid paraformaldehyde until red fumes are no longer evolved; the oxidation is complete in a few minutes. The solution is cooled, made alkaline, and heated with hydrogen peroxide (perhydrol) to destroy the paraformaldehyde; boiling decomposes the excess of hydrogen peroxide. In the test experiments described silver gauze cathodes were used; they were cleaned by digestion in cold strong hydrochloric acid. A number of rapid separations can be carried out in alkaline solution by electrolysis with a current of 3 Amp. and 4 to 5 V. with a rotating stirrer (500 R.P.M.); 0.25 gm. of zinc is deposited in 30 minutes. *Separation of Zinc from Nickel.*—The solution (less than 100 c.c.), to which 5 c.c. of perhydrol has been added, is slowly poured into a hot 50 per cent. solution of 20 to 25 grms. of potassium hydroxide, heated a short time till effervescence ceases, and electrolysed. The nickel hydroxide is subsequently dissolved in acid, and the solution electrolysed or titrated. *Zinc from Aluminium.*—The separation from large quantities of aluminium is quite satisfactory; the electrolysis is carried out as for a pure zinc solution, sufficient alkali being added to keep the alumina in solution. *Zinc from Iron (Aluminium).*—The solution is treated with sodium sulphite to reduce iron, made alkaline with potassium hydroxide, and the precipitate dissolved by cautious addition of 20 per cent. cyanide solution from a burette. Soon after the beginning of the electrolysis a saturated solution of 10 grms. of sodium sulphite is added; a second addition is required after 25 to 30 minutes (for $\text{ND100} = 3\text{A}$); anodic formation of ferricyanide is thus prevented. W. R. S.

Estimation of Manganese by means of Persulphate and Silver Nitrate.

K. Swoboda. (*Zeitsch. anal. Chem.*, 1924, 64, 156-184.)—A detailed study was made of the volumetric estimation of manganese in steel by oxidation to permanganic acid with persulphate and silver nitrate, followed by titration with arsenite. As a result, the following modification is recommended: 0.25 gm. of steel (0.5 gm. if manganese is below 0.5 per cent.) is dissolved in a 500 c.c. conical flask, in 25 c.c. of acid mixture (water 1000, nitric acid 250, sulphuric acid 40 c.c.). The red fumes are boiled off; 10 c.c. of 0.1 N silver nitrate solution, enough water to bring the volume to 200 c.c., and 4 c.c. of ammonium persulphate solution

(500 grms. per litre) are added. The mixture is boiled for 3 to 5 minutes to decompose the persulphate, the liquid cooled, and 20 c.c. of 10 per cent. potassium fluoride solution or 1.5 c.c. of strong hydrofluoric acid added. The solution is immediately titrated with the arsenite solution (0.5 gm. of arsenic trioxide and 1.5 gm. of sodium bicarbonate per litre) until colourless, or, with high manganese contents, faintly green. A steel of known manganese content is taken as the standard. The end-point in this procedure is much more easily observed; the volume of arsenite solution reacting with the permanganic acid is only four-fifths of that consumed in the usual process, the reduction proceeding to the stable manganic fluoride.

W. R. S.

Estimation of Manganese. Manganous Oxalate as a Standard. R. W. Coltman. (*Ind. Eng. Chem.*, 1924, 16, 606-609.)—Manganous oxalate is proposed as a standard in the estimation of manganese by Volhard's method, the chlorate method, and similar processes. To prepare the salt, 250 grms. of pure crystallised oxalic acid are dissolved in about 500 c.c. of hot water and a solution of 60 grms. of pure potassium permanganate is added slowly while the oxalic acid solution is kept near the boiling point. The permanganate colour disappears quickly after each addition and, finally, manganous oxalate begins to precipitate. When all the permanganate has been added the hot supernatant liquid is decanted, the precipitate washed with cold water until free from oxalic acid and then dried in a current of dry air. The salt has the composition $\text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; it is not hygroscopic, does not effloresce, and will keep indefinitely in stoppered bottles under ordinary conditions. If the oxalic acid solution is allowed to become too cold during the addition of the permanganate, some trihydrate ($\text{MnC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$) may form; in this case the washed salt must be heated with water at 90°C . until all pink colour is destroyed, and the salt again collected, washed and dried. If manganous oxalate is heated with sulphuric acid until fumes of the acid are evolved, manganous sulphate for use in Volhard's method is obtained, whilst treatment with concentrated nitric acid will give a solution of manganous nitrate for the chlorate or bismuthate method.

W. P. S.

Diphenylamine Indicator with Iron. W. W. Scott. (*J. Amer. Chem. Soc.*, 1924, 46, 1396-1398.)—Diphenylamine indicator, shown by Knop (*J. Amer. Chem. Soc.*, 1924, 46, 263) to be valuable in the titration of iron with potassium dichromate, may also be used in potassium permanganate titrations of iron. Hydrochloric acid, stannic chloride and mercurous chloride, if present, do not interfere, thus enabling potassium permanganate titrations to be made where formerly they were not possible. As suggested by Knop, several c.c. of a phosphoric and sulphuric acid mixture (15 c.c. of each increased to 100 c.c. with water) were used by the author to repress the yellow colour of (ferric) chloride. The delicacy of the reaction in permanganate titrations depends on a judicious use of the indicator. The quantity of indicator used should not exceed 0.4 c.c., and the best results are obtained by the use of 0.2 c.c. of the indicator, made according to Knop's directions (1 gm. of salt per 100 c.c. of concentrated sulphuric

acid) in solutions of iron in volumes of 100 to 250 c.c. If solutions are diluted too much, the end-point is a violet in place of a deep blue colour. A table of results is given. Diphenylamine indicator may be used in the standardisation of potassium dichromate by means of standard ferrous sulphate solution, since titrations may be done with either reagent without destroying the qualities of the indicator, the blue colour disappearing with an excess of ferrous salt, but being restored by an excess of dichromate. P. H. P.

Mechanical Separation of Polonium in Sodium Hydroxide Solution by Various Substances. J. Escher-Desrivières. (*Comptes rend.*, 1924, 178, 1713-1715).—The mechanical separation of polonium, present in sodium hydroxide solution, by an insoluble hydroxide, such as that of bismuth, and its adsorption by a particular sample of animal charcoal, depend on the number of molecules of sodium hydroxide contained in a given volume of the mixture. Traces of the hydroxide are sufficient to remove all the polonium from its solution in decinormal sodium hydroxide; the active element also undergoes rapid deposition on the walls of the containing vessel. When, however, the concentration of the sodium hydroxide is high, the polonium remains in solution. T. H. P.

Colorimetric Estimation of Nitrate Nitrogen. F. M. Scales and A. P. Harrison. (*Ind. Eng. Chem.*, 1924, 16, 571-572).—The method depends on the formation of a red coloration when a nitrate is treated with strychnine in the presence of sulphuric acid and mercuric chloride. To prepare the strychnine reagent, equal volumes of 0.5 per cent. strychnine sulphate solution in concentrated hydrochloric acid and 0.1 per cent. mercuric chloride solution in water are mixed; 25 c.c. of this mixture are added slowly to 1 gm. of magnesium powder and, when reaction has ceased, the solution is cooled and filtered. The reagent should be used within a few hours of its preparation. One c.c. of the reagent is placed in a test-tube, 5 c.c. of the test solution (*e.g.* soil extract) are added, followed by 5 c.c. of concentrated sulphuric acid; the mixture is then poured into another test tube, and the coloration obtained is compared with those produced by known amounts of nitrate treated similarly and at the same time. The comparisons need not be made immediately, but all the mixtures must be made within five minutes of each other, as the colour deepens slowly on standing. Comparative results obtained by this method and by titration as ammonia are given, the amounts of nitrate nitrogen ranging from 0.2 to 4.6 mgrms. W. P. S.

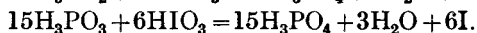
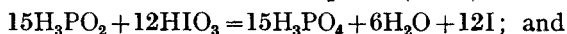
Application of the Aldehyde-Bisulphite Reaction in Volumetric Analysis A. Kurtenacker. (*Zeitsch. anal. Chem.*, 1924, 64, 56-61).—The formation of the aldehyde-bisulphite compound was found to be applicable to volumetric work in cases where the iodimetric estimation of another compound is required in presence of a sulphite. Thiosulphate may be thus titrated; two procedures were worked out. (1) If the solution is neutral towards methyl orange (*i.e.* contains bisulphite), it is treated with 5 c.c. of 35 per cent. formaldehyde, and titrated, after 5 minutes, with iodine solution. The end-point with starch is very sharp

and persists several minutes. Acid or alkaline solutions are first neutralised towards methyl orange; as this indicator interferes, the required quantity of acid or alkali is ascertained in another portion. (2) The solution, if acid, is neutralised towards phenolphthalein (conversion into sulphite). Formaldehyde is added, and the deep red colour then discharged with 10 per cent. acetic acid, of which an excess of 20 c.c. is added; the solution is immediately titrated with iodine. The author prefers the second method. The results given are very good.

W. R. S.

Iodimetric Estimation of Phosphorous and Hypophosphorous Acids.

A. Brukl and M. Behr. (*Zeitsch. anal. Chem.*, 1924, 64, 23-28.)—The solution of one of the acids, free from hydrochloric or nitric acid, is acidified with sulphuric acid and boiled with *a* c.c. of 2.5 per cent. solution of iodic acid (standardised against thiosulphate) until it is colourless and the liberated iodine completely expelled. After cooling, the excess of iodic acid is ascertained by addition of potassium iodide and titration with thiosulphate (*b* c.c.):



The quantity of iodic acid consumed by the phosphorous (hypophosphorous) acid is equivalent to one-sixth of that of the iodine indicated by (*a* - *b*). For the separation and estimation of the acids in mixtures, the solution is evaporated to dryness with a slight excess of alcoholic potassium hydroxide; the residue is transferred to a graduated 50 c.c. flask by means of alcohol. After standing for two hours, with frequent stirring, the solution is made up to the mark, filtered through dry paper, and the hypophosphorous acid estimated iodimetrically in an aliquot part of the filtrate after evaporation of the alcohol. Phosphorous acid is obtained by difference. (Potassium phosphite is soluble in alcohol to the extent of 0.0007 gm. of H_3PO_3 per 10 c.c.).

W. R. S.

Physical Methods, Apparatus, etc.

Melting Point of Coal Ash. **F. S. Sinnatt and N. Simpkin.** (*Lanc. and Cheshire Coal Res. Assoc. Bull.*, 15, 1924.)—A method has been devised for the determination of the m.p. of coal ash, so that it may be carried out on as little as 0.2 gm. of the ash. The coal is ground to pass a No. 60 sieve and incinerated in a muffle at 800-850° C., care being taken to exclude access of the products of combustion of coal gas; then the ash is ground to pass a No. 200 sieve and moistened in an agate mortar with a 10 per cent. solution of dextrin. The paste so formed is pressed through a screw press having an orifice $\frac{1}{8}$ " diameter, so that about 1" protrudes; then it is dried on a hot plate at about 250° C. and cut into pieces $\frac{5}{16}$ " in length. The furnace consists of a length of 6 inches of vitreosil tube, set in a steel-covered magnesia brick having a central aperture, so that the tube can be heated directly by an oxygen and coal-gas blow pipe. The temperature, which is regulated by controlling the oxygen supply, is observed by means of a thermocouple placed about $\frac{1}{16}$ " from the rod of ash; the m.p. is observed directly.

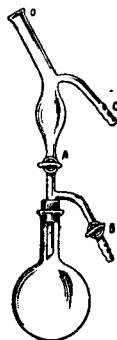
The m.p. of the ash from the separated four constituents of coal—vitrain, clarain, fusain, and durain—differs in different seams and in different horizons in the same seam within wide limits, and bears no apparent relation to its chemical composition.

H. E. C.

Identification of Phenols by means of the Spectroscope. S. Palkin and H. Wales. (*J. Amer. Chem. Soc.*, 1924, **46**, 1488-1493.)—The diagnostic value of absorption spectrum examination as a supplement to colour tests is pointed out. Azo dyes can be prepared easily with the use of the reagent diazo-*p*-nitrobenzene, which, when properly prepared, has been kept in a refrigerator for months without decomposition. The absorption spectra of azo dyes prepared from certain phenols, by coupling with azo-*p*-nitrobenzene, have been examined in three solvents, *viz.* alkaline (1) acetone, (2) alcohol and (3) water, and the data comprising absorption curves and tables of absorption-spectrum maxima are recorded for reference. The authors discuss the application of this procedure to the detection and the identification of small amounts of phenols, and a method adapted particularly to the examination of medicinal preparations is outlined. Less than 0.01 mgrm. of the phenols examined has been detected.

P. H. P.

Apparatus for Fractional Distillation under reduced Pressure. E. André. (*Bull. Soc. Chim.*, 1924, **35**, 647-648.)—This apparatus consists of a small ellipsoidal vessel the neck of which, D, is inclined and is connected with the condenser. At the side is a tubulure, C, connected with a water-pump, and at the base a tap, A, communicating with a tube on which is a side tubulure, B, also connected with a water-pump. In making a distillation the tap A is opened and the tap B closed when a large enough fraction has been collected in the small receiving flask. The tap A is then closed, and the tap B (temporarily disconnected from its water-pump) is opened, so that the air enters the receiving flask, which can then be detached. After its contents have been transferred to another vessel, the receiving flask is replaced, and the air again exhausted from it, by means of the second water pump, through the tap B. This tap is then closed, the tap A opened, and the distillation resumed. The small amount of liquid distilling during the change will have collected in the vessel above A.



Reviews.

LES ISOTOPES. Par A. DAMIENS. Pp. ix. +114. Paris: Gauthier-Villars et Cie. 1923. Price 12.50 fr.

Most of those who have lived since the time of Anaxagoras have concerned themselves but little with the constitution of matter. Epicurus, Lucretius, possibly the author of Genesis ii. 7, and Newton are honourable exceptions to this

widespread lack of interest, but it was reserved for Dalton to elaborate and systematise the conception of atoms adumbrated by these authors. That matter was continuous rather than discrete has been argued by many, and Ostwald as recently as 1903 maintained in his Faraday lecture a non-objective theory of matter. Now the atom and the quantum—the atom of action—are regarded as real entities.

The notions of atoms and elements are closely linked, and the widespread acceptance of Boyle's definition that "that was to be regarded as elementary which could not by any means be separated into different substances," and of Lavoisier's statement that one might define an element as "une substance dont le poids ne peut qu'augmenter, au cours des transformations chimique qu'il subit" led to a theoretical conception of the element, which has been found, after over a century of atomic theory, to be, in some cases, untenable.

In the 19th century chemists were so much occupied in studying the interrelations of atoms that but little curiosity was expressed as to the possibility of a complex structure of the minute infinitely hard sphere itself. The hypothesis of Prout which Stas regretfully believed that he had disproved, and the Periodic Law, the soundness of which was obvious, notwithstanding many discordant facts, were the outcome of a strong subconscious feeling in favour of the unity of matter and the necessary complexity of atoms. The discovery of spontaneously disintegrating elements and other disturbing but undoubted facts diverted the attention of mathematically minded chemists and physicists from the study of matter as such to an investigation of the atom itself, and led Rutherford and Bohr to a conception of its structure, now, in the main, accepted. This, while allowing the infinitely hard sphere to remain, showed that it must be so considered by reason, not of a solid continuity, but of the very great speed of rotation of its outer planetary electrons around a central nucleus. This speed, although too great to allow atoms to deform one another, nevertheless allows the vast majority of smaller faster-moving particles which may bombard an atom to pass through the relatively vast space within it, although some, and these the most interesting, are diverted from their linear motion by collision, attraction or repulsion, with or by the nucleus.

The work before is, as M. Perrin in his preface says "clair et agréable à lire." It sets forth the facts concerning those elements which varied evidence leads us to consider as mixtures of substances having identical chemical properties, and which Soddy has happily called *isotopes* (ἴσος same, τόπος place), as the constituents occupy the same place in the periodic table. In his first and second chapters the author relates these facts concerning the groups of radio-active elements derived respectively from uranium and thorium, showing that the end-product of each series should be, and is, lead and that many of these elements including lead, which are common to both series, should have atomic weights varying according to their origin. Soddy and others have in fact, found that, whereas ordinary lead has an atomic weight varying from 206.98 to 207.22, uranium lead varies from 206.046 to 207.10, and thorium lead

from 207.78 to 208.4. Such physical properties as density, solubility of salts, and spectra also vary, but, in the main, the two leads of atomic weight 206 and 208, as found in these various mixtures, must be as predicted on theoretical grounds, physically and chemically identical.

It is evident that atomic number, that is the number of the element in the periodic series, which is also the number of positive charges of the nucleus of the atom, and of orbital electrons around it, characterises an element chemically and physically, and that this may be different in two atoms of equal weight (isobares), or the same in two atoms of different weight (isotopes).

In the third chapter various attempts to fractionate known or supposed isotopic elements are described, and the reasons for failure in several cases are suggested. Repeated diffusion for 4 years, of hydrochloric acid gas through porous septa has yielded to Harkins and his fellow workers a gas containing chlorine of atomic weight 35.513 against the generally accepted value 35.46 and atomic weights of the constituents of 35 and 37. Kohlweiler has claimed to have obtained by diffusion an iodine of atomic weight diverging 0.66 per cent. from ordinary iodine. Unfortunately, Aston, on other grounds, has concluded that iodine is a simple element. Fractional distillation under low pressure has yielded Brönsted and Hevesy indecisive results for chlorine (hydrochloric acid was used), but marked differences for mercury.

Finally, the methods of direct frontal attack on the atom itself are discussed. In all these methods the definite relation, e/m , of the electrical charge upon an atom to its mass is used to ascertain the latter. J. J. Thomson has done this in his method of positive ray analysis by studying the characteristic parabolas made on a photographic plate by positive rays propelled by an electric discharge in a rarified gas and deviated in their headlong course by an electrical and a magnetic field. Aston, by diverging the rays in an electrical and converging them in a magnetic field, has produced "mass spectra" in which each kind of atom or molecule present has recorded its ratio e/m in orderly fashion. Metallic elements seldom yield gaseous compounds suitable for positive ray analysis, but Dempster, G. P. Thomson and Aston have successfully utilised anode rays in obtaining, by means of the vital relationship e/m , records of the masses of the different atoms associated as isotopes in some metals. By these direct methods 19 elements, up to mercury (atomic number 80), have been shown to consist each of two or more kinds of atoms, tin, for example, containing a series of 7 or 8 atoms of weights from 116 to 124. In these 19 elements certainly over 60 different kinds of atoms are to be found. With the exception of hydrogen the atomic weights found by Aston are, within an approximation of $\frac{1}{10000}$, whole numbers. All this, and much more, is told in clear simple language; 157 references to original papers are given (more than one-third of these to English publications). The illustrations are mostly taken from these papers. Three-coloured diagrams, in which isotopes are also isochromes are used to make clear the inter-relations of the radio-active elements. The author, in most cases, both arrays in some detail the evidence submitted by workers for their views and keenly criticises its adequacy.

Of what interest is this to analysts? In the first place, the study of isotopes leaves the old elements in their places in the periodic table—that is, it confirms the feeling of all chemists that those elements are chemical individuals, and shows that this is so because the atoms of differing mass in an isotopic element are in the same electrical condition. Lead appears to be the one outstanding case where differences of origin have seriously affected the statistical identity of various samples found in nature. The atomic theory has been indicated, not only as the statistical basis of analytical chemistry, but, in its extended form, as a conception closely approaching reality, whilst the soundness of Prout's hypothesis has been shown. The exact experimental work expended on atomic weights and on the newer atomicity has yielded fruits which fully justify the statement of Plato: "If arithmetic, mensuration, and weighing be taken away from any art, that which remains will not be much."

J. H. COSTE.

MANIPULATIONS DE CHIMIE COLLOIDALE. By W. OSTWALD. Translated from the 4th German Edition by E. VELLINGER. Pp. 202, 21 figs. Paris: Gauthier-Villars et Cie. 1924. Price 10 fr.

Ostwald's well-known "Kleines Praktikum" went through four editions in two years, and is recognised as an excellent manual on the practical side of Colloid Chemistry. Prof. Vellinger has made a faithful translation of this work into French. Thus, chemists, biologists, and others, able to read French better than German, will welcome this translation and find it thoroughly useful.

No fewer than 183 experiments, classed under various headings, are set out with detailed quantitative data, and they have the great merit of being guaranteed to "go." The selection of the experiments has been well made, considering the very wide field now included in colloid chemistry. Incidentally, the reviewer would prefer to see other methods included for determining surface tensions, and also a better account of the very useful flocculation-meter, in connection with which no mention is made of the work of F. V. von Hahn.

A notable omission is the very important subject of emulsions. Future editions should certainly include experiments on the making, breaking, and reversal of emulsions, and, possibly, some elementary experiments dealing with disperse systems in gases.

Colloid chemistry has many peculiarities in its methods and phenomena, and this book, an English edition of which is promised, provides a sound introduction to the practical side of a branch of science of daily-increasing importance.

W. CLAYTON.

CLOUDS AND SMOKES. By W. E. GIBBS, D.Sc. With Foreword by SIR OLIVER LODGE, F.R.S. Pp. 240. London: J. & A. Churchill. 1924. Price 10s. 6d. net.

In this book Dr. Gibbs has collected together from widely differing sources most of the available information on solids and liquids dispersed in gaseous media.

Recent work has shewn that certain types of aerosol are the counterpart in many respects of the better known and stabler hydrosols or colloidal solutions, and Dr. Gibbs has performed a very useful service in emphasising the colloid aspect of clouds and smokes and in presenting the material from the standpoint of the chemist. When, however, all has been said, our knowledge of this field, as the text shews, is surprisingly scanty, and, apart from the Brownian movement, the characteristics of these systems have scarcely been defined. Thus Chapter IV., which deals with the mechanical, thermal, optical, and electrical properties of aerosols, is suggestive but unsatisfying. Some of the deductions from first principles are unsupported by direct evidence, such as the statement on page 60 that inert dust may lower the ignition temperature of an explosive mixture of gases, or on page 61 that "the evaporation of liquid drops is arrested by the presence of an oil film."

Further, the evidence from many authors is accepted without any critical discussion of their conclusions, but this reflects the unsatisfactory state of our knowledge rather than any want of discrimination on the part of the author. The absence of definite information on the adsorption of gases by smoke particles is a case in point. Adsorption may be the main factor in determining the stability of many systems, but no quantitative measurements are available.

The mechanism of thermal precipitation, again, raises many interesting questions, but since Aitken's work little has been done. The intensity of light radiated from small particles is a subject in which fresh experimental work is needed. Bancroft has pointed out the disagreement between the work of Tolman on smokes and that of Mecklenberg on suspensions of sulphur. In most smokes the sizes of the particles lie well below the wave-length of sodium light and in a region where the two effects of reflection and scattering are difficult to disentangle.

The electrical character of smokes is very obscure. Undoubtedly, ionisation of the surrounding medium is largely responsible for the charges on the particles, but it is unknown whether smokes, as a whole, are electrically neutral, or whether preferential adsorption of ions takes place to any extent. Smokes produced by chemical reactions at low temperatures contain, initially at least, very few charged particles, but it is not known whether this proportion changes with time, and whether an equilibrium is reached between molecules, free ions, and adsorbed ions. In other words, is there a definite contact potential between a smoke particle and the surrounding medium?

These and many other questions are suggested on reading the first half of this book. It is clear that there is here a large field awaiting investigation, and Dr. Gibbs' treatment cannot fail to stimulate interest in this little explored region of disperse matter.

The second half of the book treats of the practical and industrial aspects of clouds and smokes. The subjects dealt with range over meteorological phenomena, smoke filtration and precipitation, dust explosions, and chemical warfare. A

good account is given of the Lodge-Cottrell process and its applications, and the difficulty experienced in precipitating certain smokes, which the author ascribes to the reflection of ions, shews again how little the fundamental behaviour of aerosols is understood.

Dr. Gibbs is to be congratulated on a very complete review of the whole literature of the subject; copious references are given, and this monograph, which is the only work of its kind, will appeal both to the chemical engineer and the student of pure science.

R. WHYTLAW GRAY.

MONOGRAPHS ON MINERAL RESOURCES, WITH SPECIAL REFERENCE TO THE BRITISH EMPIRE. Prepared under the direction of the Imperial Institute. VANADIUM ORES. London: John Murray. 1924. Price 5s. net.

The general preface explains the object of this series of monographs—"to give a general account of the occurrences and commercial utilisation of the more important minerals, particularly in the British Empire. No attempt has been made to give details of mining or metallurgical processes."

This little monograph gives a short historical account of vanadium, a description of the principal ores, their occurrence, the views held as to their genesis, and an indication as to where vanadium ores are being raised at the present time.

A commendable feature is that the volume contains a bibliography of the references used in the compilation of the monograph. This in itself has a marked value.

Amongst comprehensive references to sources of supply, the description of the famous deposit at Quisque, now the world's chief source of vanadium, which "has contributed about 80 per cent. of the world's production," has extreme interest; for the discovery, in 1905, that that which was formerly considered to be coal, was in reality an asphaltite associated with the mineral "patronite" (which contains vanadium as $V_2S_5 + 4S$) is one of the romances of modern mining.

It may have interest to add that, in addition to deposits mentioned in S. America—Argentina, Chile, and Peru, there is a further deposit at the extreme north, namely Venezuela, upon which the Reviewers did considerable work many years ago. The ash of this particular asphaltite carried 11.0 per cent. of V_2O_5 and 1.86 per cent. of NiO.

For the layman, the uses of the metal and a brief outline of its metallurgy are presented; for the student or professional worker, the material here compiled will be found to be reliable. As a general survey of vanadium deposits, the vicissitudes of their workings in various localities, and as some account of the causative factors for the same, this book fulfils a useful purpose.

GEO. R. THOMPSON.
JOHN MYERS.