

No. 1100

THE ANALYST:

THE ORGAN OF THE
Society of Public Analysts and other
Analytical Chemists

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT
OF ANALYTICAL CHEMISTRY

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VOL. XLV.

1920

TRADE AGENTS:

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2, 4, 6, 8, ORANGE STREET, LONDON, S.W.

1920



THE ANALYST.

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

ORDINARY MEETING, DECEMBER 3, 1919.

HELD at the Chemical Society's Rooms, Burlington House. Dr. Samuel Rideal, President, in the chair.

A certificate was read for the first time in favour of Mr. William John Read, M.Sc., F.I.C.

Certificates were read for the second time in favour of Messrs. Percy Ewart Bowles, F.I.C., Ph.D. (Heidelberg), Charles Crowther, M.A. (Oxon), Ph.D. (Leipsic), John William Hawley, B.Sc. (Lond.), A.I.C., Ernest Joseph Lush, B.A. (Cantab.), A.I.C., H. Percy Marks, B.Sc., A.I.C., Robert Selby Morrell, M.A. (Cantab.), Ph.D. (Wurzburg), F.I.C.

The following were elected Members of the Society: Messrs. John Dalton and William Norman Leng.*

The following papers were read: "New Distillation Method for Detecting Adulteration in Butter and for Estimating Fats of the Coconut Group," by George Van B. Gilmour, B.Sc. (Lond.), A.R.C.Sc.I., A.I.C.; "A New Process for the Determination of Arsenic, with Notes on the Chemistry of the Marsh-Berzelius Process," by B. S. Evans, M.C., B.Sc., F.I.C.

The Council's nominations of Officers and Council for 1920 were read as follows:
President: Alfred Smetham.

Past-Presidents Serving on the Council: Messrs. Leonard Archbutt, Edward J. Bevan, A. Chaston Chapman, Bernard Dyer, Otto Hehner, Samuel Rideal, E. W. Voelcker, J. Augustus Voelcker.

Vice-Presidents: W. J. A. Butterfield, G. N. Huntly, G. R. Thompson.

Hon. Treasurer: Edward Hinks.

Acting Hon. Treasurer: E. W. Voelcker.

Hon. Secretaries: P. A. Ellis Richards, E. Richards Bolton.

Other Members of the Council: Messrs. F. W. F. Arnaud, W. Bacon, F. H. Carr, H. G. Colman, G. D. Elsdon, P. J. Fryer, R. Hellon, H. Hurst, C. A. Keane, S. E. Melling, G. W. Monier-Williams, W. Lincoln Sutton.

* Andrew More, F.I.C., was elected a member on November 5, 1919.

A NEW METHOD FOR DETECTING ADULTERATION IN BUTTER AND FOR ESTIMATING FATS OF THE COCONUT GROUP.

By GEORGE VAN B. GILMOUR, B.Sc. (LOND.), A.R.C.Sc.I., A.I.C.

(Read at the Meeting, December 3, 1919.)

THE chief difference between this method and those now in general use is in the treatment of the volatile acids. This method separates the volatile acids into two groups, depending on their solubility or insolubility in saturated brine.

Three numbers are obtained from which is deduced the genuineness of the fat under examination.

The test is carried out as follows:

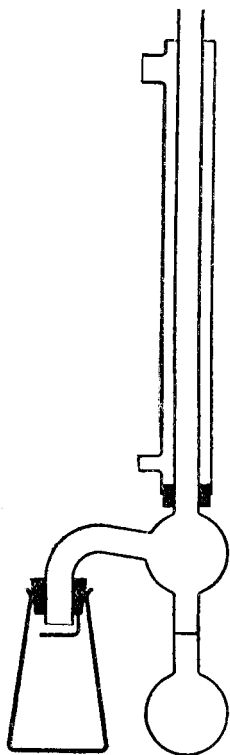
Twenty grms. of the clear filtered fat are saponified in a 300 c.c. resistance conical flask with 30 grms. of glycerol and 8 c.c. of 50 per cent. aqueous caustic potash; a few small pieces of porous porcelain are also added. The heating can be done over a naked Bunsen flame. The soap is made up to 200 c.c. with distilled water. To 50 c.c. are added 100 c.c. of a solution of sulphuric acid containing

12.5 grms. of concentrated acid per litre, and 0.1 gm. of pumice powder that has been sifted through butter muslin.

The distillation is carried out in the Blichfeldt distillation apparatus* shown in the diagram, which is calibrated to hold 100 grms. of water at 65° C., the source of heat being an electric heater regulated to distil to the mark in about twenty minutes. When the distillate has been collected, the apparatus is disconnected, and 0.5 c.c. of 1 per cent. phenolphthalein and $\frac{N}{10}$ NaOH (a few c.c. in excess of that which is necessary to neutralise all the acids in the distillate) are added through the condenser tube. The openings are corked and the contents well shaken. At the commencement of the shaking the cork is temporarily released to reduce the pressure inside. The contents are then removed to a 200 c.c. measuring flask and cooled to about 15° C. The excess of alkali is titrated with $\frac{N}{10}$ H₂SO₄, and the number of c.c. of $\frac{N}{10}$ NaOH, equivalent to the total volatile acids is obtained by difference: from this is subtracted 0.4 to allow for a blank, and the corrected figure is represented by T.

Up to this stage the procedure is identical with that described by Blichfeldt (*J. Soc. Chem. Ind.*, 1919, **38**, 150-152T).

To the measuring flask containing the neutral soap is now added a volume of $\frac{N}{10}$ H₂SO₄ equal to that of $\frac{N}{10}$ NaOH required to neutralise the total volatile acids (T+0.4), and after this are added 61 grms. of pure dry sodium chloride (the salt used should be neutral to phenolphthalein, otherwise a slight correction will be necessary)



* The complete apparatus can be obtained from F. E. Becker and Co., Hatton Wall, London, E.C. 1.

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The flask is corked and well shaken to dissolve the salt, the volume being made up to 200 c.c. The contents of the flask are next filtered, and 190 c.c. of the filtrate titrated with $\frac{N}{10}$ NaOH: no further indicator need be added, as phenolphthalein is already present.

The number of c.c. of $\frac{N}{10}$ NaOH required is multiplied by $\frac{20}{19}$ and from this is subtracted 0.4 for a blank. The number obtained represents the soluble volatile acids, and is indicated by S. T - S gives the number I, which represents the insoluble volatile acids. The following example shows how the results are tabulated.

$\frac{N}{10}$ NaOH added to the distillate	c.c. 26.0
$\frac{N}{10}$ H ₂ SO ₄ required to neutralise excess of alkali	4.4
	21.6
Deduction for blank experiment	0.4
	21.2
$\frac{N}{10}$ NaOH required for total volatile acids (T)	21.2
$\frac{N}{10}$ H ₂ SO ₄ added to liberate volatile acids	21.6
$\frac{N}{10}$ NaOH required to neutralise volatile acids dissolved in 190 c.c. saturated brine	3.3
$\frac{N}{10}$ NaOH required to neutralise volatile acids dissolved in 200 c.c. saturated brine $3.3 \times \frac{20}{19}$	3.5
Deduction for blank experiment	0.4
	3.1
$\frac{N}{10}$ NaOH required for volatile acids soluble in saturated brine (S)	3.1
$\frac{N}{10}$ NaOH equivalent to volatile acids insoluble in saturated brine (T - S = I)	18.1

T = 21.2 ; S = 3.1 ; I = 18.1.

Saturated brine was adopted after experimenting with brines of different strength. The solubility of the fatty acids was found to decrease with increased concentration of brine.

Below are given figures illustrating this :

Grms. of NaCl in 200 c.c.	S for Butter Fat.	S for Coconut Fat.	S for Palm Kernel Fat.
61	22.5	1.6	1.1
40	24.6	—	—
20	26.1	3.7	2.1

Results obtained by the above method for butter, coconut, palm kernel and babassu fats :

T represents total volatile acids.

S represents volatile acids soluble in saturated brine.

I represents volatile acids insoluble in saturated brine.

Twelve Samples of Butter from Different Sources.

Sample.	T.	S.	I.
1.	27.2	20.4	6.8
2.	29.3	22.0	7.3
3.	26.3	20.3	6.0
4.	28.6	21.8	6.8
5.	30.1	22.8	7.3
6.	30.4	22.5	7.9
7.	29.4	22.0	7.4
8.	26.4	21.1	5.3
9.	31.0	22.5	8.5
10.	31.4	22.8	8.6
11.	32.2	23.3	8.9
12.	29.1	22.2	6.9

Six Different Samples of Coconut Fat.

1.	20.3	1.5	18.8
2.	19.7	1.6	18.1
3.	22.0	1.7	20.3
4.	21.0	1.5	19.5
5.	20.4	1.6	18.8
6.	21.3	1.7	19.6

Six Different Samples of Palm Kernel Fat.

1.	12.8	1.1	11.7
2.	13.1	1.2	11.9
3.	13.8	1.3	12.5
4.	12.4	1.0	11.4
5.	12.8	1.0	11.8
6.	12.0	1.0	11.0

A Sample of Babassu Fat gave the following figures :

	14.3	1.2	13.1
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Variations for butter, coconut and palm kernel fats :

<i>Butter Fat.</i>		<i>Coconut Fat.</i>		<i>Palm Kernel Fat.</i>	
T.	From 26.0 to 33.0	T.	From 19.5 to 22.5	T.	From 12.0 to 14.0
S.	20.0 ,, 23.5	S.	1.3 ,, 1.8	S.	1.0 ,, 1.3
I.	5.0 ,, 9.5	I.	18.0 ,, 20.7	I.	11.0 ,, 12.7

Below are given results for—

- (1) Mixtures of butter fat with coconut and palm kernel fats.
- (2) Pure fats used in (1).
- (3) Theoretical figures that the mixtures (1) should give calculated from (2).

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	T.	S.	I.
(1) Butter fat + 5 per cent. coconut fat	28.3	20.0	8.3
" " 10 " " " " " " " " " "	27.8	18.8	9.0
" " 20 " " " " " " " " "	26.9	17.0	9.9
" " 5 per cent. palm kernel fat	27.9	20.2	7.7
" " 10 " " " " " " " " "	27.3	19.1	8.2
" " 20 " " " " " " " " "	25.7	16.8	8.9
(2) Butter fat	28.7	21.0	7.7
Coconut fat	21.0	1.5	19.5
Palm kernel fat	13.1	1.2	11.9
(3) Butter fat + 5 per cent. coconut fat	28.3	20.0	8.3
" " 10 " " " " " " " " "	27.9	19.0	8.9
" " 20 " " " " " " " " "	27.1	17.1	10.0
" " 5 per cent. palm kernel fat	27.9	20.0	7.9
" " 10 " " " " " " " " "	27.1	19.0	8.1
" " 20 " " " " " " " " "	25.6	17.0	8.6

The following are results for—

- (1) Mixture of arachis oil with coconut and palm kernel fats, and of arachis oil, butter and coconut fats.
- (2) The pure fats used in (1).
- (3) Theoretical figures that the mixtures (1) should give calculated from (2).

	T.	S.	I.
(1) 50 per cent. arachis oil + 50 per cent. coconut fat ...	11.1	1.3	9.8
50 " " " " palm kernel fat	8.0	0.8	7.2
70 " " " 30 per cent. coconut fat	7.8	1.0	6.8
70 " " " " palm kernel fat	4.7	0.7	4.0
30 per cent. coconut fat + 60 per cent. arachis oil + 10 per cent. butter fat	10.7	2.9	7.8
30 per cent. coconut fat + 65 per cent. arachis oil + 5 per cent. butter fat	8.7	1.8	6.9
(2) Butter fat	30.9	22.5	8.4
Coconut fat	22.0	1.7	20.3
Palm kernel fat	13.8	1.3	12.5
Arachis oil	1.0	0.3	0.7
(3) 50 per cent. arachis oil + 50 per cent. coconut fat ...	11.5	1.0	10.5
50 " " " " palm kernel fat	7.4	0.8	6.6
70 " " " 30 per cent. coconut fat	7.3	0.7	6.6
70 " " " " palm kernel fat	4.8	0.6	4.2
30 per cent. coconut fat + 60 per cent. arachis oil + 10 per cent. butter fat	10.3	2.9	7.4
30 per cent. coconut fat + 65 per cent. arachis oil + 5 per cent. butter fat	8.8	1.8	7.0

Interpretation of the figures obtained by the method :

Genuine butters have been found to give figures which agree with one of the following conditions :

	Soluble.	Insoluble.
1.	20.0 to 21.0	Below 7 (usually 6-7)
2.	21.0 „ 22.5	„ 8.0
3.	22.5 „ 23.5	„ 9.5

When butter is adulterated with coconut or palm kernel fat the soluble volatile acids from either of them affect the soluble figure only very slightly—viz., by about 0.15 for each 10 per cent. of coconut fat, and 0.11 for each 10 per cent. of palm kernel fat present. The soluble figures for butters adulterated with these fats can thus be assumed to decrease approximately in proportion to the amount of either fat present.

The insoluble volatile acids from coconut and palm kernel fats affect the insoluble figure of a butter adulterated with these fats by about 1.9 for each 10 per cent. of coconut and 1.2 for each 10 per cent. of palm kernel fat present.

The insoluble figures for butters vary between 5 and 9.5, therefore on addition of coconut or palm kernel fat the butter portion of the insoluble figure will decrease by 0.5 to 0.9 for each 10 per cent. of these fats present, but, at the same time, the portion of the insoluble figure due to coconut or palm kernel fat will cause an increase respectively of 1.9 and 1.2. The result is that a butter adulterated with increasing quantities of these fats will give soluble figures that consistently fall, and, at the same time, insoluble figures that consistently rise. Butter adulterated with fats that do not give rise to volatile acids will give figures both soluble and insoluble reduced in proportion to the amount of adulteration.

The amount of adulteration is calculated in the following way :

Using average figures for pure butter, coconut, and palm kernel fats, the following three equations have been worked out, from which can be calculated directly the percentage of any one of the fats present in a mixture :

$$(1) \text{ Per cent. butter fat} = 4.67 S - 0.35 I = x.$$

$$(2) \text{ Per cent. coconut fat} = 5 I - 0.38x.$$

$$(3) \text{ Per cent. palm kernel fat} = 7.69 I - 0.59x.$$

Should butter fat be absent from the mixture the second terms of the equations (2) and (3) vanish.

For differentiating between coconut and palm kernel fats see the paper by S. H. Blichfeldt (*loc. cit.*).

Distillation figures for mixtures of known composition showing results calculated from the above equations :

Actual Composition.				T.	S.	I.	Calculated from Equations.		
Butter Fat per Cent.	Coconut Fat per Cent.	Palm Kernel Fat per Cent.	Arachis Oil per Cent.				Butter Fat per Cent.	Coconut Fat per Cent.	Palm Kernel Fat per Cent.
10	90	—	—	21.2	3.1	18.1	8.1	87.4	—
95	—	5	—	27.9	20.2	7.7	91.6	—	5.2
5	30	—	65	8.7	1.8	6.9	6.0	32.2	—
10	30	—	60	10.3	2.9	7.4	10.9	31.8	—
—	—	50	50	8.0	0.8	7.2	—	—	55.4
50	5	—	45	15.7	10.7	5.0	48.2	6.7	—
40	15	—	45	14.8	8.6	6.2	38.0	16.6	—
10	60	—	30	15.9	3.0	12.9	9.5	60.9	—

There is considerable difference between the maximum and the minimum figures that can represent the total volatile acids in butter. The result of this is that a butter with a high figure can be adulterated with up to 10 per cent. of lard or other fat that does not give rise to volatile acids, without the figure being reduced below the lower limit. Such cases of adulteration cannot be detected by the distillation tests: if the butter is suspected, other tests must be applied.

Of the methods in use for detecting adulteration in butter and for estimating fats of the coconut group, those of Kirschner-Polenske and Blichfeldt are the most reliable. In the "Maypole" laboratory the latter method has been preferred. This new method has been tested against Blichfeldt's, and has been found simpler and somewhat more exact; a complete estimation can be made in about an hour.

It has been noticed that the ratio of soluble to insoluble silver salts in the Blichfeldt process is to some extent dependent on the quantity of fatty acids present. This might also be true in the Kirschner process. The fact that, by using saturated brine, the ratio of soluble to insoluble volatile acids is not affected by the quantity of the acids present, is a point very strongly in favour of the method.

THE LABORATORY,

MAYPOLE MARGARINE WORKS, LTD., SOUTHALL, MIDDLESEX.

DISCUSSION.

Mr. BOLTON remarked that he could not criticise the efficiency of the process without studying the figures which he had only just seen for the first time. He felt that, in order to judge the value of this new method, the figures should be tabulated side by side with those obtained by the standard Reichert-Meissel-Polenske-Kirschner method, in order to distinctly prove the advantages claimed. The standard Reichert-Meissel-Polenske-Kirschner method would detect and even estimate 1 per cent. of butter fat in the presence of coconut oil and palm-nut oil.

If the method now put forward would do this more accurately or more rapidly than it would be for the analyst to decide if it was worth while to scrap the great number of published figures for the standard method, and to obtain fresh standards for the author's method.

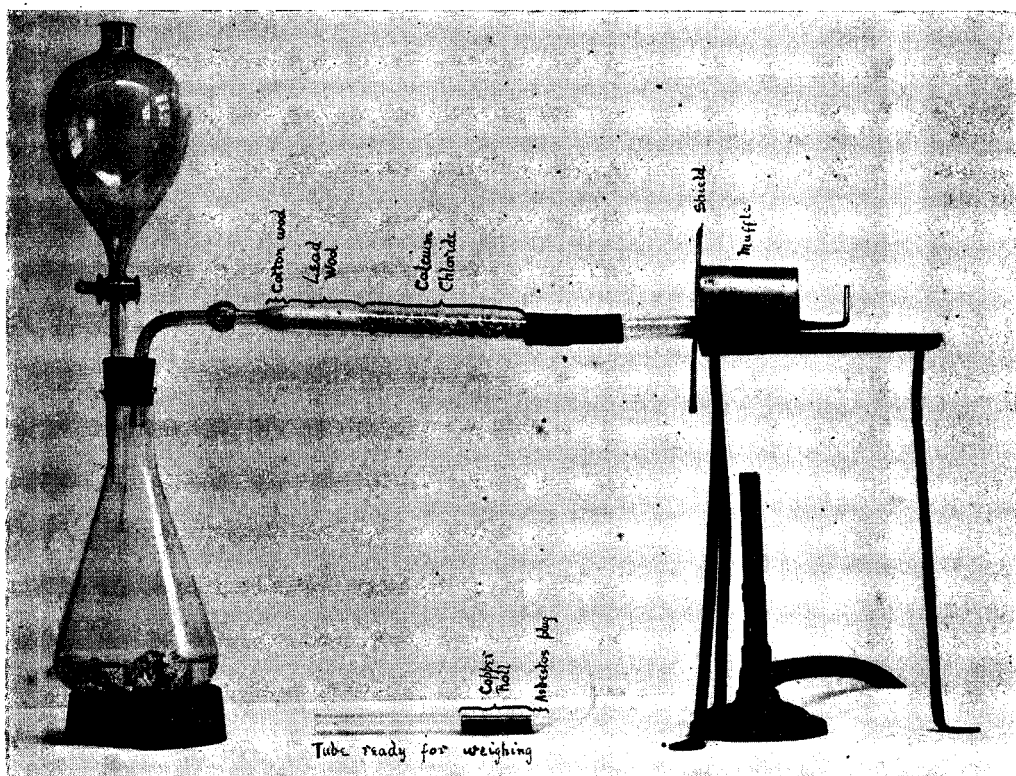
A NEW PROCESS FOR THE ESTIMATION OF ARSENIC, WITH NOTES ON THE CHEMISTRY OF THE MARSH-BERZELIUS PROCESS.

BY B. S. EVANS, M.C., B.Sc., F.I.C.

(Read at the Meeting, December 3, 1919.)

THE process about to be described was worked out to provide a rapid gravimetric method of estimating arsenic in organic compounds.

General Principles.—The arsenic is evolved as AsH_3 , which is passed over ignited copper, the gain in weight of the copper being a measure of the amount of arsenic present.



DETAILS: (a) *Apparatus.*—The apparatus required is practically that used in the Marsh-Berzelius test. A flask, containing zinc coated with cadmium, as in Chapman's modification, closed with a double-bored rubber stopper carrying a tapped funnel and a tube containing wool soaked in lead acetate and dried and granulated calcium chloride; to this drying tube is attached, by means of a piece of vulcanised rubber tubing, a tube similar to that used in the Marsh-Berzelius test, but the drawn out portion of which is only about 2 inches long, the last inch or so being turned up.

It has been found convenient, and, in the long run, much cheaper, to have this drawn out tube made of silica, as it not only retains its shape when heated, but also can be used repeatedly (the work carried out for this paper was all done with one tube which was still perfectly good after considerably over one hundred estimations). Hard glass can, however, be used with quite good results.

(b) *Dimensions of Apparatus :*

Flask	capacity about 250 c.c.
Weight of zinc	40 to 50 grms. coated with cadmium by heating with a solution containing about 1 grm. of a cadmium salt.
Length of wide part of silica tube up to shoulder	about 12 cms.
Internal diameter of wide part of silica tube	0.9 cm.
Length of wide portion of drying tube	15 to 16 cms.
Internal diameter of wide portion of drying tube	1.2 cms.

These dimensions are those that happen to be convenient, but they have no special significance.

(c) *Process.*—A piece of thin sheet copper, about 4 inches by 1, and weighing about 2 grms., is heated to redness in the Bunsen flame, and allowed to cool; it is then formed into a little tube about an inch long by rolling round a glass rod. Into the silica tube is pushed a small fragment of asbestos wool (which first must be thoroughly ignited to drive off water), and it is pressed into place right up against the shoulder of the tube where it has been drawn out, which shoulder it should be just big enough to plug loosely. The copper tube is now dropped into the silica tube, and the latter is attached by means of a rubber connection to the drying tube. The silica tube is supported horizontally over a Bunsen burner, the portion where the copper is placed being covered by a little sheet iron muffle about $1\frac{1}{2}$ inches long, and a shield, made of asbestos card with a slot cut in it, is hung on to the silica tube, where the muffle ends, to protect the rubber connection from the heat of the burner.

Dilute sulphuric acid is now run in through the tapped funnel, and when the hydrogen evolved has displaced all the air in the apparatus, the jet and the burner are lighted, the burner being so placed as to heat that portion of the tube where the copper tube is to bright redness. The apparatus is allowed to run for two or three minutes, the burner is then turned out, and the tube is allowed to cool. When thoroughly cool, the silica tube is disconnected from the apparatus, the hydrogen replaced by air by connecting it for a moment to a filter pump, and it is weighed. After weighing, it is reconnected to the apparatus, the hydrogen started again with a little dilute sulphuric acid, and the burner and jet relighted. When the tube is again red hot the solution containing the arsenic to be estimated is run in through the tapped funnel, care being taken not to introduce any air, and the funnel is rinsed with water.

10 EVANS: A NEW PROCESS FOR THE ESTIMATION OF ARSENIC, WITH

The arsenic coming off in the form of arseniuretted hydrogen is completely retained by the copper, forming a lustrous silver white arsenide. Even if the hydrogen is evolved fast enough to cause a jet flame of an inch or more in height, not a trace of arsenic gets through, the colour of the flame affording a sensitive indicator, as the slightest trace of arsenic produces the lilac discoloration. After the test solution has all been added, the apparatus is kept running for forty-five minutes by the addition of small quantities of strong sulphuric acid (owing to the pressure in the apparatus it is best to force this in by blowing through a tube passing through a cork in the mouth of the tapped funnel). The height of the jet flame should be kept as near $\frac{1}{2}$ inch as possible. At the end of forty-five minutes the burner is turned out, and when the tube is quite cold it is disconnected, and, the hydrogen having been displaced by air as before, it is again weighed. The difference between the two weights divided by 0.986 gives the amount of arsenic added to the apparatus. The amount of arsenic present for the test should be 0.05-0.50 grm. calculated as As_4O_6 .

There is no need to clean out the silica tube between tests: all that is needed is to drop out the copper and replace by a fresh roll. The same asbestos plug serves for many tests, and is, in fact, better after being used once or twice, owing to a slight danger of its not having been completely dehydrated by the first ignition. Iron and many heavy metals interfere with the estimation, and, if present, they must be separated, preferably by distillation of the arsenic.

To test the method, several estimations were carried out on different amounts of pure arsenious oxide, with the following results:

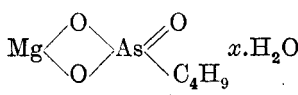
As_4O_6 taken. Grm.	As_4O_6 found. Grm.	Percentage of Arsenic recovered.
0.0750	0.0740	98.66
0.0750	0.0740	98.66
0.2030	0.1996	98.33
0.2274	0.2243	98.60
0.2634	0.2592	98.42
0.3078	0.3044	98.91
0.5030	0.4966	98.72

As a check on the purity of the arsenious oxide used, the arsenic in it was estimated both by the magnesium arsenate method and by the iodine titration method, with the following results:

$Mg_2As_2O_7$ method	...	Mean of four analyses, 100.17 per cent.
Titration	99.59 ..

From these results it would seem that the sample was practically pure arsenious oxide, and consequently the factor 1/0.986 was adopted to correct the results of the method.

The following table shows the results obtained by this method in the analysis of a variety of arsenic compounds. The organic compounds were in all cases oxidised by Thomson's method, published in the *British Food Journal*, October, 1902; the sample of arsenic trichloride was treated in the same way, and it may be noted that no loss of arsenic resulted. The second column gives the percentage of arsenic calculated direct from the gain in weight of the tube; the third column this number divided by 0.986; the last column the theoretical percentage:

Compound.	Arsenic found, per Cent.	Arsenic corrected by 0.986 Factor, per Cent.	Arsenic calculated, per Cent.
As(C ₆ H ₅) ₂ Br	{ 23.87 23.86	{ 24.21 24.20	24.27
AsC ₆ H ₅ Br ₂	23.46	23.79	24.04
C ₃ H ₇ AsBr ₂ (crude) ...	25.59	25.95	26.99
" (purified)	26.45	26.83	26.99
" (another purified sample)	26.72	27.09	26.99
C ₄ H ₉ AsBr ₂ (crude) ...	24.72	25.07	25.68
" (purified)	25.17	25.52	25.68
C ₄ H ₉ AsCl ₂	36.36	36.87	36.95
(C ₆ H ₅) ₂ AsCl	27.77	28.16	28.35
C ₆ H ₅ AsO	43.83	44.45	44.65
Pure elemental arsenic ...	98.45	99.84	100.00
AsCl ₃ *	{ 41.11 41.03	{ 41.69 41.61	41.33
 $x \cdot H_2O$	—	26.35	26.28 calculated from Mg.

In conducting the estimation of arsenic by the Mg₂As₂O₇ method, some facts concerning that process came to light.

Since the textbooks differed considerably among themselves as to the amount of the solubility factor to be allowed for the filtrate and washings, it was decided actually to estimate the arsenic left in solution, by the method described in this paper; the procedure adopted was as follows: The arsenate was precipitated in accordance with the directions of the textbooks, and washed with dilute ammonia, the filtrate and washings being measured and preserved. The precipitate was then dissolved in hydrochloric acid, and reprecipitated with ammonia, filtered through a Gooch crucible, washed as before, ignited to Mg₂As₂O₇, and weighed, the filtrate and washings, as before, being measured and kept. The two filtrates were evaporated separately (except in one instance, where they were mixed), acidified, reduced with SO₂, and run off by the method described in this paper.

* The sample was contaminated with a trace of As₄O₆. One per cent. of As₄O₆ would account for the excess As found.

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The results obtained are shown in the following table :

Weight of As_2O_3 taken.	Weight of $Mg_2As_2O_7$ obtained.	First Filtrate. Vol. Arsenic.	Second Filtrate. Vol. Arsenic.	Percentage of Arsenic—				
				From Pre- cipitate.	From Filtrate.	Total.		
0.2964	0.4548	133 c.c.	0.0006	185 c.c.	0.0044	98.02	2.23	100.25
0.2072	0.3142	369 c.c.	0.0050	Filtrates mixed		96.85	3.19	100.02
0.1554	0.2292	175 c.c.	0.0014	225 c.c.	0.0055	94.21	5.86	100.07
0.3136	0.4672	217 c.c.	0.0024	248 c.c.	0.0098	95.17	5.13	100.30

Two points are sufficiently clear from these results : (a) The second filtrate, containing no magnesia mixture, dissolves almost four times as much arsenic as the first, although the volume is very little greater. (b) The amount of arsenic remaining in solution is not by any means so negligible as some textbooks infer. By applying certain solution factors it is possible to arrive at a correct result, yet it must be largely due to chance, unless the volumes of both filtrates and both sets of washings are carefully watched.

The missing 1.4 per cent. in the copper-tube method still remains rather a mystery, although a good deal of work has been done to trace it. A variety of possibilities suggest themselves, and were examined : (a) The missing amount of arsenic might be precipitated in the flask, either as element or as an arsenide. (b) A proportion of arsine might remain in solution. (c) The arsenic might go into solution as a non-reactive complex. (d) A proportion of arsine might diffuse through the rubber connections. (e) A proportion of arsine might be decomposed in passing through the lead wool and calcium chloride. (f) A proportion of arsine might escape from the apparatus altogether, not being held by the copper. (g) The loss might be due to steady loss of weight by the silica tube and the copper.

A, b, and c were tested in several experiments, of which the following is typical : 0.5152 gm. of As_2O_3 was run off and 97.59 per cent. was recovered (0.3809 gm. of As). A black precipitate of elemental arsenic separated on the top of the liquid in the flask (this, as will be shown later, is apt to happen when too much arsenic is used). The test was run until all the zinc was dissolved. The liquid was filtered, the precipitate treated with strong nitric acid, which completely dissolved it ; 5 c.c. strong sulphuric acid were added, and the solution was evaporated till the sulphuric acid fumed ; it was then diluted with water, reduced with sulphur dioxide, and run off ; an amount of arsenic corresponding to 1.38 per cent. was recovered (0.0054 gm. As). The original filtrate containing the zinc sulphate was evaporated down with fuming nitric acid and strong sulphuric acid and digested for several days, taken up with water, reduced, sulphuretted hydrogen passed through all night, the precipitate filtered off, boiled with nitric acid and 5 c.c. strong sulphuric acid to fuming-point of the sulphuric acid, taken up with water, reduced, and run off.

The amount of arsenic recovered was 0.0002 gm., corresponding to 0.05 per cent. Results : 97.59 per cent. + 1.38 + 0.05 = 99.02, total percentage of As recovered.

This and other similar experiments, using different methods of attack, but always with the same results, seemed to show that if the arsenic remained in the flask at all it was as a singularly obstinate complex.

To test *d*, the question whether arsine could diffuse through the rubber connection, the ordinary rubber connection in which the silica tube was pushed right up to the drying tube, was replaced by a length of about a foot of rubber tubing, on the assumption that far more diffusion should take place under these circumstances. Amount of As_4O_6 taken, 0.2952 grm. ; weight of As recovered, 0.2202 grm. ; corresponding to 98.47 per cent.

To test *e*—*i.e.*, whether the lead wool or CaCl_2 caused decomposition of the AsH_3 —the drying tube was replaced by one 5 feet long, packed with lead wool and CaCl_2 in the same proportions, on the assumption that far greater decomposition should take place with greater length. Amount of As_4O_6 taken, 0.1974 grm. ; weight of As recovered, 0.1480 grm. ; corresponding to 98.97 per cent.

Another test was made with an ordinary drying tube in which the lead wool was replaced by ordinary cotton-wool. Amount of As_4O_6 taken, 0.2410 grm. ; weight of As recovered, 0.1804 grm. ; corresponding to 98.81 per cent.

With regard to *f*, the non-coloration of the hydrogen flame, and its failure to deposit arsenic on cold porcelain, were taken as proof that no arsenic was lost by passing out of the apparatus.

With regard to *g*, the various blank tests invariably showed agreement, within the errors of weighing, between the weights of the tube before and after running.

The compound formed with the copper usually melts and has a solder-like appearance, but, occasionally, brilliant silver-white blade-shaped crystals are formed.

Some analyses were attempted :

	Cu.	As.	Total.
Crystalline crust detached from copper ...	70.50	29.27	99.77
Button of arsenide exposed to large excess of AsH_3	67.50	32.28	99.78
Calculated from increase in weight of copper when fully saturated with arsenic ...	70.23	29.77	100.00
Calculated from formula Cu_3As ...	71.78	28.22	100.00
Calculated from formula Cu_5As_2 ...	67.95	32.05	100.00

It would seem as if we were here dealing with a mixture of arsenides.

Although of course it is impossible to draw rigid conclusions as to the behaviour of the minute amounts of arsenic usually looked for by the Marsh-Berzelius test, it yet seemed worth while to investigate the chemistry of that process from the point of view of the larger amounts here involved, where quantitative results could be obtained.

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In the first place, it is interesting to note that insensitive zinc is a difficulty that occurs in this process, just as it does in the Marsh-Berzelius test, and that it can be overcome by the same means. In the early days of the process, the zinc was used without cadmium; a batch of zinc, however, came to hand, which gave low results; on coating this zinc with cadmium the difference in the results disappeared.

The following figures were obtained—one set with As_4O_6 , another with elemental As, and a third with impure $\text{As}(\text{C}_4\text{H}_9)_3$:

	As_4O_6 per Cent. of As_4O_6 .	As.	$\text{As}(\text{C}_4\text{H}_9)_3$ per Cent. of Arsenic.
Untreated zinc	92.60	93.15	27.78
Zinc coated with cadmium	98.60	98.45	28.88

What happened in the flask throws some light on, at any rate, one function of the cadmium. With both coated and uncoated zinc, very shortly after the addition of the arsenic to the flask, there was a brown coloration of the liquid, followed by the separation of a scum of metallic arsenic on the surface. In the case of the untreated zinc, this scum remained substantially unchanged at the end of the test, and undoubtedly represented the loss of the arsenic.

In the case of the treated zinc, the scum remained unchanged for some time; then (after about twenty minutes run), as generally happens, the cadmium sponge became detached from the zinc and floated up to the surface. As soon as the cadmium came in contact with the floating arsenic the latter began to disappear, and soon no trace of it was left. It would seem that what happens is that the arsenic and cadmium form an electric couple with the cadmium as anode and the arsenic as cathode, the cadmium dissolves, and the nascent hydrogen coming off from the arsenic combines with it to form arsine. Later work showed that the separation of elemental arsenic is a fairly common occurrence. If the amount of As_4O_6 in the flask much exceeds 0.5 gm. it seems invariably to occur, and therefore it is desirable to keep the amount of arsenic below that limit; the majority of salts, too, if present in sufficient amount, also cause a separation of arsenic; unless, however, the amount separated is excessive, the cadmium sponge, if it floats up properly, should easily deal with it. If from any cause undissolved arsenic should be left at the end of the test, it is necessary to filter it off, dissolve in strong nitric acid, add 5 c.c. of strong sulphuric acid, take down to the fuming-point of the sulphuric acid, take up with water, reduce with sulphur dioxide, and, after the latter has been boiled off, run off again, adding this result to the first one. An example is the following: Amount of As_4O_6 taken, 0.7318 gm.; percentage, calculated from first run, 94.84; percentage, calculated from second run, 3.75; total, 98.59.

A few observations were made which have a bearing on this separation of arsenic:

(a) Some powdered arsenic (element) was added to the flask, the jet being lighted but not the burner. The arsenic colour appeared in the jet flame at once,

but this colour markedly increased when the cadmium floated up and came in contact with the arsenic. (b) Some zinc was added to a solution of As_4O_6 in sodium bicarbonate; it slowly became coated with a brown film. On adding a little acid, a considerable amount of arsenic separated out. (c) Most of the zinc used in this work was sufficiently pure to cause the hydrogen to come off slowly and with difficulty. It was repeatedly noticed that addition of a solution of pure As_4O_6 caused an immediate rush of gas, just as the addition of a copper salt would.

From these observations it would appear that the first action when As_4O_6 is added to zinc and acid is a reduction to elemental arsenic on the surface of the zinc. Here it forms an electric couple with the zinc, the arsenic being the cathode. The nascent hydrogen coming off from the surface of the arsenic combines with it forming arsine. If, however, strong solutions of salts, which are known to cause the stripping of films, are present, or if the amount of arsenic is sufficient to cause a weakly adherent film, the latter is stripped and, being carried up to the surface, is removed from further action until the cadmium touches it.

In view of the disturbing effect of various substances on the sensitiveness of the Marsh test, it seemed worth while to determine the effect of varying amounts of them on the process under consideration, and, if possible, discover the cause of their interference.

Copper was the first metal selected. The method adopted was to keep the amount of arsenic approximately constant, and add varying amounts of copper sulphate; the amount of arsenic recovered was calculated as a percentage of the amount added; the amount of arsenic retained by the copper was calculated from the difference between the percentage recovered and 98.6. In every case there seemed to be a catalysis of the As_4O_6 —As reaction, and a considerable amount of arsenic separated on the surface; this, however, was always completely removed by the cadmium sponge. In addition to this, black particles separated in the liquid, remaining at the end of the test, when all the zinc and cadmium was dissolved, as a black powder at the bottom of the flask. This powder was filtered off, washed and weighed, and, in two or three cases, was approximately analysed: it appeared to be a copper arsenide of the approximate composition, Cu_3As . There was apparently no metallic copper left.

Weight of As_4O_6 .	Weight of Cu.	Weight of Arsenide and Insoluble Matter from Zn.*	Weight of As recovered.	Per Cent. of As recovered.	Weight of As lost.	Weight of As in Arsenide.
0.1996	0.0166	0.0533	0.1476	97.61	0.0015	0.0144
0.1996	0.0332	0.0670	0.1439	95.17	0.0052	
0.1998	0.0499	0.0846	0.1398	92.36	0.0094	
0.2003	0.0665	0.1036	0.1378	90.80	0.0118	
0.2002	0.4158	0.5574	0.0928	61.19	0.0567	

* This column includes any matter in the zinc insoluble in sulphuric acid, and is therefore only a rough approximation.

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It would seem, therefore, that copper prevents the formation of arsine in two ways: (a) By formation of copper arsenide; (b) by causing the separation of a large amount of elemental arsenic.

The cadmium causes the conversion of the separated arsenic into AsH_3 , unless the amount is excessive, but it is powerless to deal with the arsenide, though there is a certain amount of evidence to show that AsH_3 is given off very slowly from the arsenide.

The results obtained with iron were more difficult of interpretation. The iron was added in the form of ferrous sulphate, the other conditions being the same as in the copper experiments. The separation of arsenic in the flask was, if anything, more marked, and there was again a formation of arsenide in the form of a fine black powder. The arsenide was filtered off and weighed, but analyses of it were unsatisfactory. In all cases it was found that the great bulk of the iron remained in solution.

The following results were obtained:

Weight of As_2O_3 .	Weight of Fe.	Weight of Arsenide and Insoluble Matter in Zn.	Weight of As recovered.	Percentage of As recovered.	Weight of As retained.
0.2016	0.0193	—	0.1506	98.60	—
0.2003	0.0967	—	0.1450	95.57	0.0046
0.1996	0.1450	0.0388	0.1460	96.54	0.0031
0.1994	0.2418	0.0448	0.1325	87.72	0.0164
0.2004	0.4835	0.0746	0.1202	79.20	0.0295
0.1998	2.0144	0.1280	0.0760	50.20	0.0733

The most noteworthy thing about these results is that, although by far the greater part of the iron remains in solution, the amount of arsenic retained is approximately proportional to the amount of iron present, and the curve total iron—arsenic retained is very nearly a straight line, so also is the curve total iron—arsenide formed. This is all the more surprising in that, on attempting the analysis of the arsenide residues they were found to contain varying amounts of lead, which was at last traced to the cadmium salt used in coating the zinc; the cadmium salt had, however, been previously used for a large number of tests, and no lead arsenide or retention of arsenic had been observed before, so that the iron apparently brought about combination between the lead and the arsenic.

Weight of As_2O_3 .	Weight of Fe.	Weight of Arsenide.	Weight of As recovered.	Percentage of As recovered.	Weight of As retained.
(a) Contaminated Cd 0.2016	1.113	Not weighed	0.1278	83.70	0.0228
(b) Purified Cd 0.2010	1.113	0.0404	0.1196	78.56	0.0305

Iron alum was tried in place of ferrous sulphate, once using the contaminated cadmium salt, and once using the same salt purified from lead; the results only complicated the matter further.

It will be noticed that considerably more arsenic was retained with the pure cadmium salt than with that which contained lead. Lead was present in the arsenide from (a), and was absent from that from (b).

The effect of a few other substances on the evolution of AsH_3 was tried, the results being expressed as percentages recovered (uncorrected by the factor 0.986) of the amount of arsenic taken.

Weight.	Substance.	Weight of As_2O_3 added.	Percentage recovered.
10 grms.	Na_2HPO_4	0.1988	98.68
10 "	ZnSO_4	0.2000	98.77
10 "	Na_2SO_4	0.2012	98.42

The blank due to the substance, where necessary, was subtracted. These results show that the three substances used exerted no retaining effect.

Some work done on tin salts seemed to show that they did not exercise a retaining action, but the salts were so impure that the figures are not given.

I should like to express my thanks to Professor J. F. Thorpe and to Dr. Whiteley, of the Imperial College of Science, where this work was done, for suggestions and criticisms; and to the Chemical Warfare Department for permission to publish it.

DISCUSSION.

Dr. DYER said that it was common experience that much of the "pure" zinc now obtainable was too pure to be sensitive, even with the use of cadmium solution. This fault he had found could be corrected by alloying the zinc with about 0.2 per cent. of copper. Zinc thus alloyed was, of course, in itself, quite "insensitive." But when cadmium was used with it, it became very sensitive, and was also sufficiently brisk in its action with hydrochloric acid. Much of the trouble experienced by workers with the Marsh-Berzelius process was due to unsatisfactory calcium chloride, much of that now obtainable being strongly absorptive of arseniuretted hydrogen, especially if used for more than two experiments.

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NOTE.

The Editor desires 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.

DESICCATED COCO-NUT.

In Messrs. Bolton and Revis's book "Fatty Foods," the following sentence relating to desiccated coco-nut occurs: "When examining this product the presence of sugar, starch, etc., must be sought for as adulterants."

A few months ago I analysed a sample of desiccated coco-nut, with the following results: Moisture, 3.87 per cent.; fat, 67.00 per cent.; sugar, 6.67 per cent. (by Fehling after inversion), 7.5 per cent. (by polarimeter). There was practically no copper-reducing power before inversion.

I was inclined to think that sugar had been added, as no mention is made by Messrs. Bolton and Revis of cane sugar being naturally present. Mr. C. E. Sage confirmed the amount of cane sugar present in the sample, but was of the opinion that the sugar was naturally present.

I analysed samples of desiccated coco-nut, copra, and fresh coco-nut, with the following results:

(1) Fresh coco-nut, milk, 1.5 per cent. cane sugar (by polarimeter); solid portion, after washing, 4.63 per cent. cane sugar on sample, 9.2 per cent. cane sugar on dry matter.

(2) Fresh coco-nut, solid portion: 6.16 per cent. cane sugar on sample, 13.5 per cent. on dry matter. No reducing sugar was present in either sample.

Copra (received from Dr. Dyer): Dextrose, 2.4 per cent.; cane sugar, 0.95 per cent.

Copra (received from Mr. Sage): Dextrose, 0.77 per cent.; cane sugar, 7.71 per cent.; moisture, 0.66 per cent.

Desiccated Coco-nut:

1. Purchased: Dextrose, traces only; cane sugar, 4.48 per cent. (4.5 per cent. on dry matter).

2. Received from Mr. Sage: Moisture, 3.3 per cent.; dextrose, nil; cane sugar, 4.56 per cent. (5.2 per cent. on dry matter).

From these figures it is evident that desiccated coco-nut may contain as much as 7 per cent. cane sugar.

E. Bourquelot (ANALYST, 1904, 29, 330) gives the composition of two samples of commercial Indian sugar; one prepared from the milk of the coco-nut contained 74.95 per cent. of cane sugar.

The amount of cane sugar present in desiccated coco-nut no doubt depends on whether the solid portion has been well washed or not before desiccating.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Simple Method for Measuring the Acidity of Cereal Products: Its Application to Sulphured and Unsulphured Oats. V. Birekner. (*J. Agric. Research*, 1919, 18, 33-49.)—Of the methods proposed by other workers, that of Schindler has been much used in America (*Zeitsch. Landw. Versuch.*, 1909, 12, 721-756). The material is extracted for sixteen to eighteen hours at normal temperature with neutral alcohol (sp. gr. 0.86), and the filtrate titrated with standard alkali. The author finds the chief deficiencies of this method to be the following: (1) Lack of a definite end-point in titration; (2) the values obtained with raw unsulphured cereals are always too high; (3) the values for sulphured cereals (oats) are too low; (4) the increase in acidity caused by sulphuring often appears as an actual decrease owing to incomplete extraction of the acid; (5) expense due to use of pure alcohol. In place of this prolonged alcohol extraction it is proposed to employ ice water for one hour (oats), or one and a half hours for maize. About 15 grms. of the sample are used for each estimation, the whole being well shaken every fifteen minutes, and kept at a temperature of 1 to 2° C., both during the extraction and while filtering. Phenolphthalein is used as an indicator, and results are expressed as the "acidity value," which is the number of c.c. $\frac{N}{1}$ alkali required to neutralise the extract from 1,000 grms. of material; for the actual titration 25 c.c. of the filtrate is titrated with $\frac{N}{20}$ sodium hydroxide.

Unsulphured oats by this method show acidity values ranging from about thirteen to twenty, while sulphured oats rise to about thirty or more. It also appears that the amount of acid present in oat kernels does not change markedly during the early stages of spoilage. Sulphur-bleached oats showed no increase in acidity upon prolonged standing in the ground state when tested by the ice-water method, since the acid-forming ferments present in the grain are destroyed by the sulphur fumes. With Schindler's method pronounced increases in the acid values were observed in such cases owing to the continued formation of certain protein cleavage products, which in aqueous solution are amphoteric, but in alcohol solution are acid. Ice water extracts of oats or maize if filtered and kept at 1 to 2° C. for twenty-four hours without being neutralised undergo no change in acidity, but, if neutralised, a new formation of acid takes place notwithstanding the low temperature. H. F. E. H.

Crismer Value of Butter Fat. L. Vandam. (*Ann. Falsific.*, 1919, 12, 260-269.)—The alcohol used in determining the Crismer value (critical temperature of solution in alcohol) of butter fat should have a sp. gr. of 0.7976 at 15° C., corresponding to 99.1 per cent. of alcohol by weight, and the strength of the alcohol should be tested from time to time by means of a standard mixture of petroleum and vaseline. The critical temperature of solution of this mixture in 99.1 per cent. alcohol is determined once for all, and, by its use, the strength of fresh quantities of

alcohol may be ascertained. If an alcohol containing more or less than 0.9 per cent. of water is employed, the results obtained must be corrected in order to give the correct Crismer value. To the value obtained is added the following correction for each 0.1 per cent. of water below or above 0.9 per cent.: From 0 to 0.4 per cent., +1.0; 0.5 to 0.8 per cent., +0.9; 1.0 to 1.1 per cent., -0.9; 1.2 to 2.3 per cent., -0.8; 2.4 to 2.9 per cent., -0.7. If the butter fat under examination is not neutral, a correction for the acidity must be added to the Crismer value; this correction is the number of c.c. of $\frac{N}{10}$ sodium hydroxide solution required to neutralise 4 grms. of the butter fat.

W. P. S.

Estimation of Added Water in Milk. J. Goldan. (*Ann. Chim. anal.*, 1919, 1, 342-345.)—The "simplified molecular concentration constant," when corrected for the volume of casein and fat as described by Ferris (*ANALYST*, 1918, 43, 35) is a trustworthy constant for the detection of added water in milk. The author has not met with a genuine milk having a value below 70, the average value being 74.

W. P. S.

Estimation of Gelatin, contained, together with Coagulable Proteins, in Feeding-Stuffs, etc. H. Wagner and G. Schöler. (*Landw. Versuchs-Stat.*, 1918, 92, 171-180; through *J. Soc. Chem. Ind.*, 1919, 38, 841A.)—Five grms. of the substance are boiled with 200 c.c. of water for five hours in a 300 c.c. Erlenmeyer flask, a larger flask being employed only with materials which "bump." The whole is then transferred to a 500 c.c. measuring flask, cooled, made up to volume, and filtered. If absence of dissolved protein in the filtrate is shown by failure of the reaction with acetic acid and potassium ferrocyanide, and of the xanthoprotein reaction, the nitrogen in 100 c.c. of the filtrate, corresponding with 1 gm. of the substance, is determined by the Kjeldahl method: this represents gelatin- plus amide-nitrogen. Another quantity of 100 c.c. of the filtrate is treated in a 250 c.c. measuring flask with 40 c.c. of 10 per cent. tannin solution (the nitrogen-content of which is determined by a blank experiment), the liquid being made up to volume, mixed, allowed to settle overnight, and filtered. The nitrogen in 200 c.c. (0.8 gm. of substance) or 150 c.c. (0.6 gm.) of the filtrate is determined by the Kjeldahl method: the result, corrected for the nitrogen of the tannin solution, gives the amide-nitrogen, and subtraction of this from the gelatin- plus amide-nitrogen yields the gelatin-nitrogen alone. The method has been tested with mixtures of blood-albumin and gelatin, and is found to give satisfactory results. A number of different feeding-stuffs have been analysed by the method.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Toxicity of Cacao Shell. Marchadier and Goujon. (*Ann. Falsific.*, 1919, 12, 283-287.)—Several French Army horses died after being fed with cacao shell and cacao shell powder in place of oats. The animals received 1.5 kilos. of the substance per day for four days before their death. Since cacao shell may contain up to 0.9 per cent. of total alkaloids (caffeine and theobromine), the horses may have taken

daily some 13 grms. of alkaloid, or over 50 grms. in all. The animals undoubtedly died as the result of alkaloidal poisoning. It is considered that cacao shell is a dangerous fodder; if the alkaloids are extracted previously, the cacao shell loses its food value owing to the simultaneous removal of other extractives. W. P. S.

Detection of Hydrocyanic Acid in Cases of Poisoning. L. Chelle. (*Comptes rend.*, 1919, **169**, 852-854.)—It has long been known that hydrocyanic acid cannot be detected in the organs of the body a short time after death. Experiments described in detail show that this is due not to the disappearance of the hydrocyanic acid, but to its fixation by the sulphur compounds produced during cadaveric putrefaction and its conversion into thiocyanic acid. This acid remains in the residue when the finely divided material is distilled with water and phosphoric acid to separate hydrocyanic acid, and the latter may be quantitatively recovered by treating the residue with a suitable oxidising agent such as sulpho-chromic acid. Further experiments have shown that thiocyanic acid is not formed in the ordinary process of putrefaction. C. A. M.

ORGANIC ANALYSIS.

New Method for Estimating the "Copper Value" of Cellulose and the Valuation of the Quality of Cellulose. E. Hägglund. (*Papierfabr.*, 1919, **17**, 301-305; through *J. Soc. Chem. Ind.*, 1919, **38**, 895A.)—Schwalbe's method for the estimation of the copper value may be simplified by using Bertrand's volumetric method for the titration of the reduced cuprous oxide. Four grms. of the finely disintegrated cellulose are stirred with 200 c.c. of water, which is then heated to boiling, and 100 c.c. of boiling Fehling's solution added. The mixture is boiled for fifteen minutes, and then filtered in a "Neubauer platinum crucible," or else on a double filter paper with the assistance of kieselguhr paste. The cellulose containing the cuprous oxide is washed with hot water, and then treated with 100 c.c. of boiling ferric sulphate solution containing 50 grms. of ferric sulphate and 200 grms. of sulphuric acid per litre. The iron solution should previously be tested for inertness towards permanganate. The cuprous oxide is thereby dissolved, and the cellulose is washed several times with boiling water. The filtrate is then titrated with $\frac{N}{10}$ permanganate, and shows a sharp end-point from green to pink. With regard to tests for the quality of unbleached Mitscherlich sulphite pulp, the author has determined the copper sulphate absorption values, but finds no connection between these and the bleaching capacity of the pulps. The bleaching quality, however, shows a more consistent relationship with the lignin value as determined by Klason's method. None of the usual chemical tests, such as copper value, hydrolysis value, etc., showed any satisfactory concordance with the strength and mechanical qualities of the cellulose. Only in certain very pronounced cases can any definite relation be found between the tensile strength and the degree of digestion of the pulp. It may frequently happen that a fully digested pulp is as strong as or stronger than an under-digested material.

Estimation of Cyanogen Compounds in Concentrated Ammonia Liquor.

Part II. The Estimation of Thiocarbonate. P. E. Spielmann and H. Wood. (*J. Soc. Chem. Ind.*, 1919, **38**, 369-370T).—A method described previously by the authors (*ANALYST*, 1919, **44**, 143) for the estimation of cyanogen compounds in ammonia liquor has been extended to include the estimation of thiocarbonate which is usually present in the liquor. The method now proposed depends on the fact that digestion for forty-five minutes at 70°-75° C. will convert thiocarbonate completely into thiocyanate without affecting the cyanide, and that ammonium polysulphide at 30°-35° C. will convert cyanide into thiocyanate in thirty minutes without attacking the thiocarbonate. The estimations are carried out as follows, 25 c.c. of the ammonia liquor being used in each case: *Thiocyanate*.—As described previously (*loc. cit.*). The solution should be cooled with ice during the addition of the sulphuric acid. *Cyanide and thiocyanate*.—The liquid is digested at 30° C. for thirty minutes with an excess (2 c.c.) of ammonium polysulphide. *Thiocarbonate and thiocyanate*.—The liquid is diluted with 15 c.c. of water, 10 c.c. of concentrated ammonium polysulphide are added, and the mixture is heated at 75° C. for forty-five minutes. *Ferrocyanide*.—This is estimated from the amount of "blue" obtained in the estimation of the thiocyanate and of the thiocarbonate and thiocyanate. If, on acidifying the solution after digestion, precipitated sulphur obscures the red coloration formed by the addition of iron alum, an excess of the latter should be added, the mixture heated at 40° C., and filtered. Large quantities of hydrogen sulphide and slimy precipitated sulphur, formed after the polysulphide treatment, may be removed by a preliminary shaking with lead carbonate. In the above estimations the flasks containing the reacting substances should be provided with loose stoppers in order to exclude atmospheric oxygen. Some experiments were made on the removal of thiocarbonate from ammonia liquor, although this is not required in the above methods. It was found that if the liquor was shaken with lead carbonate, filtered, and the filtrate shaken with zinc carbonate, the whole of the thiocarbonate could be removed without affecting the thiocyanate, which remained in solution as a zinc salt. On boiling the filtrate, ammonia was expelled and zinc oxide separated out and was removed by filtration. The preliminary treatment with lead carbonate avoided the production of an excessive amount of zinc sulphide.

W. P. S.

Electrometric Method for the Estimation of Ferrocyanides. G. L.

Kelley and R. T. Bohn. (*J. Amer. Chem. Soc.*, 1919, **41**, 1776-1782).—Ferrocyanides may be estimated by determining the change in the oxidation potential during titration with permanganate, with the aid of apparatus similar to that previously described, and with the addition of a voltmeter (*ANALYST*, 1916, **42**, 108; 1917, **43**, 373). About 1 gm. of potassium ferrocyanide is dissolved in 250 c.c. of water, the solution acidified with 2.5 to 5.0 c.c. of sulphuric acid (sp. gr. 1.58), and titrated with $\frac{N}{20}$ permanganate solution. The permanganate solution is added slowly, with constant mechanical stirring, and finally, as the end-point is approached, drop by drop, and time is allowed for the completion of the reaction. The end-point is taken as the greatest change in potential corresponding to the addition of equal

amounts of permanganate solution. If the end-point has been passed, the solution may be titrated back with standard ferrocyanide solution. Ferricyanides, or chlorides, up to 1 grm. of sodium chloride or its equivalent, do not interfere with the estimation, but salts which form precipitates with either ferrocyanide or ferricyanide must not be present.

C. A. M.

Physical Properties of Mannite and its Aqueous Solutions. J. M. Braham. (*J. Amer. Chem. Soc.*, 1919, **41**, 1707-1718.)—It is recommended that the following values, based on experimental determinations and comparison with the most trustworthy recorded results, should be adopted as physical constants of mannite in place of those given in the textbooks: Melting-point, 166.05°C .; specific rotation, $[\alpha]_{\text{D}}^{25^{\circ}\text{C}} = -0.244^{\circ} \pm 0.002$ and $[\alpha]_{\text{D}}^{25^{\circ}\text{C}} = -0.208 \pm 0.002$ (calculated); sp. gr., 1.487 (room temperature); specific heat, $C^{(25-100^{\circ})} = 0.327_{\gamma}$ and $C^{(14-26^{\circ})} = 0.315$; and heat of combustion, 4.00 cal./gram. The solubility in water (100 c.c.) was found to be as follows: At 0°C ., 10.36; at 20°C ., 18.6; at 50°C ., 47.6; at 80°C ., 115.0; and at 100°C ., 197.0 grms.

C. A. M.

Modification of the Phenylhydrazine Method of Determining Pentosans. P. Menaul and C. T. Dowell. (*J. Ind. and Eng. Chem.*, 1919, **11**, 1024-1025.)—A method for the estimation of furfural may be based on the precipitation of the furfural with phenylhydrazine and the estimation of the excess of phenylhydrazine in the filtrate by oxidation. Experiments in this direction showed that a quantitative evolution of nitrogen could be obtained by the action of ammoniacal copper sulphate, provided chlorine or other halogen ion were absent. The distillation was therefore carried out with sulphuric acid instead of hydrochloric acid, using sodium sulphate instead of sodium chloride to lower the solubility of the precipitate. During the distillation the volume in the flask was kept practically constant by the addition of water. Phenylhydrazine was added to an aliquot portion of the distillate, agitation for the necessary time being effected by bubbling carbon dioxide through it. A portion of the filtrate from the hydrazone was introduced by means of a dropping funnel into a 250-c.c. Fresenius nitrogen bulb which had previously been filled with ammoniacal copper sulphate and heated to expel the air. A 100-c.c. burette was connected to the tube of the Fresenius bulb, and a glass tube provided with a stop-cock connected the neck of the bulb with a Schiff's nitrometer containing sulphuric acid. The measured portion of the filtrate was brought into the bulb through the dropping funnel by closing the cock leading to the nitrometer and lowering the burette. The bulb was then heated so as to keep the reaction mixture near the boiling-point until the reaction was complete. The results by this method coincided exactly with those by the phloroglucinol method, and the time required for an estimation of the excess of phenylhydrazine in the filtrate is only about twenty minutes.

J. F. B.

Method for the Direct Estimation of Naphthalene in Tar, Tar Oil, and Crude Naphthalene by Conversion into its Pierate. Knoblauch. (*J. Gasbel.*, 1918, **61**, 136-137, 145-149; through *Chem. Zeit. Rep.*, 1919, **43**, 247.)—The alcoholic

solution of the substance is treated at 60° C. with an excess of solid picric acid, and the heating continued until all is in solution. The mixture is then cooled slowly, diluted with 0.3 per cent. picric acid solution to 120 c.c., the precipitated picrate collected on a filter, and washed with 0.2 per cent. picric acid solution. The filter is folded over the precipitate, pressed slightly, placed in a beaker, 80 c.c. of water are added, and the picric acid titrated with $\frac{N}{10}$ sodium hydroxide solution, using methyl-orange as indicator. A small correction must be made for the amount of picric acid wash-water retained by the filter-paper.

W. P. S.

Estimation of Unsaponifiable Substances in Crude Materials for Soap Manufacture. Herbig. (*Seifenfabr.*, 1919, 39, 174; through *Chem. Zeit. Rep.*, 1919, 43, 239.)—Goldschmid's method of estimating unsaponifiable substances in soap material (*Seifenfabr.*, 1918, 38, 41-42) may be modified by making the first extraction by shaking with 100 c.c., the second with 50 c.c., and the third and fourth extractions with 20 to 30 c.c. of ether. The colour of the ethereal extract does not necessarily indicate that unsaponifiable substances are present, since in test experiments the percentage results agreed, although the last extract was still coloured. As a rule, two extractions (by shaking) with ether are sufficient, but in the case of certain kinds of fats three or four extractions are necessary.

C. A. M.

Estimation of Volatile Fatty Acids. G. Wiegner and J. Magasanik. (*Chem. Zeit.*, 1919, 43, 656.)—The authors discuss the question of the distillation of volatile fatty acids and the connection between the concentration of a fatty acid-water mixture and its vapour pressure, and state that a vapour-pressure curve for a propionic acid-water mixture, constructed by Konowaloff, does not agree with results obtained by Duclaux and by the authors themselves. For a distillation interval in which the fatty acid and water vapour pressures alter linearly, the following equation applies: $\log y = k \log x + 2 - 2k$, where y is the quantity of acid in the distillation residue expressed as a percentage of the original amount of acid, x the quantity of water in the residue expressed as a percentage of the original amount, and k a constant. A new graph is suggested in place of the Duclaux curve, the abscissæ being the difference of the logarithms of the quantities of water in the distillation residue, and the ordinates the difference of the logarithms of the quantities of acid in the residue; k may be found from this graph. In homologous series and for dilute solutions, k increases by 0.6 for each additional CH_2 group in the molecule. The constant, therefore, increases as the fatty acids become less soluble, or, in other words, the least soluble acids are the more volatile in steam. If 2 per cent. solutions of the fatty acids are distilled until the volume is reduced by one-half, the following quantities of the different acids, respectively, will be found in the distillate: Formic acid, 22.7 per cent.; acetic acid, 36.6 per cent.; propionic acid, 58.5 per cent.; *n*-butyric acid, 73.8 per cent.; *n*-valeric acid, 82.4 per cent.; *n*-caproic acid, 88.2 per cent.; *n*-caprylic acid, 94.8 per cent.; *n*-capric acid, 97.7 per cent. For the distillation of acetic acid at 25° to 30° C. under 14 mm. pressure, $k = 0.287$. Steam distillation of fatty acids, when the volume of water, w , is kept constant, follows the

equation $\log y + \frac{kx}{w} = 2$, where y is the residual percentage of acid, x the grms. of water vapour, and k the constant.

W. P. S.

INORGANIC ANALYSIS.

Electrometric Analysis with Potassium Ferrocyanide. E. Müller. (*Chem. Zeit.*, 1919, **43**, 597.)—Electrometric titration with potassium ferrocyanide solution fails in the case of many metals owing to the fact that the precipitated ferrocyanide is not of definite composition. Lead and zinc may, however, be titrated accurately by this method; there is a sharp change in potential for the compounds $\text{Pb}_2\text{Fe}(\text{CN})_6$ and $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$. In the case of zinc, the end-point is more sharply denoted by the change in potential than by the use of uranium nitrate as an external indicator.

W. P. S.

Method for the Analysis of Nitrous Gases. A. Geake and F. J. Squire. (*J. Soc. Chem. Ind.*, 1919, **38**, 367-369r.)—The following method is described for the analysis of gases in a system of absorption towers used in connection with a plant for the denitration of nitroglycerin spent acid. The gases consisted of a mixture of nitric oxide and peroxide, carbon monoxide and dioxide, oxygen, and nitrogen. The sampling device consisted of a glass bottle of known capacity, and of such size that the sample of gas contained about 0.3 gm. of nitrogen oxides. The bottle was closed with a stopper, through which passed a tapped glass tube, the diameter of the bore of the tap and of the outer portion of the tube being 2 to 3 mm. The portion of the tube inside the bottle was bent so that it nearly touched the wall of the bottle near the shoulder. Twenty-five c.c. of $\frac{N}{10}$ permanganate solution and 1 c.c. of concentrated sulphuric acid were placed in the bottle, the air exhausted from the latter, and the tap then closed. To take the sample of gases, the tube was inserted in the sampling hole and the bottle tilted, so that the permanganate solution covered the end of the tube inside the bottle. The tap was then opened for one second (but not long enough to completely fill the bottle with the gases) and then closed. The volume of the residual gases in the bottle at atmospheric pressure was determined by connecting the tapped tube with an Orsat apparatus, the burette and levelling tube of which were filled with mercury, then making the measurement in the usual way. The portion of the gases drawn into the Orsat apparatus was used for the estimation of carbon dioxide (absorption in sodium hydroxide) and oxygen (by phosphorus). The residual gas in the apparatus was taken as being nitrogen; actually it contained carbon monoxide, but as this is inactive and has the same density as nitrogen its presence was unimportant. Air was then admitted to the sample bottle, the permanganate solution titrated with ferrous sulphate solution, and the total combined nitrogen estimated as described by Bowman and Scott (*ANALYST*, 1915, **40**, 474).

W. P. S.

Colorimetric Determination of Lead Dioxide in Litharge. W. V. Morgan. (*J. Ind. and Eng. Chem.*, 1919, **11**, 1055.)—Lead dioxide in litharge

may be determined approximately by noting the intensity of the colour produced by the oxidation of aniline. The method is also applicable, with slight alterations, for the determination of oxidising agents in general where they occur as an impurity in non-oxidising agents. A definite amount of litharge—*e.g.*, 5 grms., is boiled for a minute with a solution containing 2 grms. of aniline hydrochloride in 10 c.c. of water and 5 c.c. of concentrated hydrochloric acid. The solution is then cooled to separate any lead chloride which has formed, and the deposit is filtered off. It is not necessary to convert the whole of the litharge into lead chloride, as the action depends on the oxidising power of the dioxide only. The colour of the filtrate is compared with that produced by known quantities of lead dioxide. J. F. B.

Separation of Iron, Aluminium, Chromium, Glucinum, Titanium and Zirconium by Means of Sodium Carbonate. P. Wenger and J. Wuhrmann. (*Ann. Chim. anal.*, 1919, 1, 337-339.)—The method is the same in principle as that described previously by Wenger and Wunder (*ANALYST*, 1912, 37, 373) for the separation of aluminium from glucinum (beryllium). The ignited and weighed oxides are mixed in a platinum crucible with six times their weight of sodium carbonate, and the mixture is kept in a state of fusion for two hours. After cooling, the mass is boiled with water, the insoluble portion collected on a filter, ignited, and again fused with sodium carbonate and extracted with boiling water. The aqueous solution (filtrate) now contains the aluminium and chromium in the form of sodium aluminate and sodium chromate, respectively. The aluminium is precipitated as hydroxide by treating the boiling solution with an excess of ammonium nitrate, added in small portions at a time, and is separated by filtration. The chromate in the filtrate from the aluminium hydroxide is reduced by alcohol and precipitated as hydroxide by ammonia. The portion remaining insoluble after fusion with sodium carbonate contains the iron, titanium, zirconium, and glucinum as oxides. If titanium is present it is impossible to separate the iron and zirconium oxides by treatment with hydrochloric acid (1 : 1), since the presence of this metal causes a part of the zirconium oxide to pass into solution; this method of separation, however, may be applied in the case of iron and zirconium oxides alone. Further, iron and titanium oxides may be separated by any of the usual methods, even in the presence of glucinum, provided that zirconium oxide is not also present. Iron and glucinum oxides may be separated by fusion with potassium bisulphate and subsequent treatment with potassium hydroxide solution. W. P. S.

Method for Estimating Phosphorus in Steel containing Vanadium. J. Maitchell. (*Chem. News*, 1919, 119, 212.)—Two grms. of the steel are weighed into a 500 c.c. flask, and, when dissolved in 90 c.c. of nitric acid (sp. gr. 1.2), $\frac{N}{10}$ potassium permanganate is run in until a permanent precipitate of manganese oxide is formed. The whole is then cooled to below 20° C., and $\frac{N}{10}$ ferrous ammonium sulphate is added until the solution is bright green, and all the brown precipitate is dissolved. Twenty c.c. of ammonia (sp. gr. 0.96) are then added, and the solution shaken until the precipitated ferric hydroxide is all redissolved,

care being taken to keep the whole below 20° C. Sixty c.c. of faintly ammoniacal ammonium molybdate solution are next added, and, after closing the flask with a rubber bung, the whole is vigorously shaken for three minutes, after which the solution is allowed to stand for twenty to thirty minutes. To prevent the vanadium coming down with the phosphomolybdate and giving a dark orange precipitate, the solution must be kept below 20° C. The molybdate precipitate is next filtered off, washed free from acid, shaken up in 80 c.c. of water and estimated by running in excess of standard caustic soda, and titrating back with sulphuric acid and phenolphthalein. The whole determination can be done in three-quarters of an hour, unless the carbides are difficult to get into solution. Analyses are adduced, showing the great accuracy of the method as applied to test mixtures. H. F. E. H.

Deroode Method for Determining Potash. T. E. Keith and H. E. Shiver. (*J. Ind. and Eng. Chem.*, 1919, 11, 1049-1052.)—In a previous paper the authors had shown (*ANALYST*, 1918, 43, 236) that the Lindo-Gladding method gives low results for water-soluble potash in certain cases, and that the Deroode method afforded a simpler and more accurate procedure without the use of platinum apparatus. The validity of the method has now been further investigated in relation to the possible presence of sodium nitrate, ammonium salts, and high percentages of phosphates and organic matter. The Deroode method (*ANALYST*, 1898, 23, 278) as finally applied is carried out as follows: Ten grms. of material are transferred to a 500 c.c. flask, 300 c.c. of water added, boiled for thirty minutes, cooled, made up to the mark, and filtered through a dry filter, the first runnings being discarded. An aliquot portion of 50 c.c. is placed in a thin porcelain dish of 200 to 250 c.c. capacity, and 30 c.c. of *aqua regia* are added after putting the dish on the hot plate. After evaporating to dryness another 30 c.c. of *aqua regia* are added and again evaporated to dryness; the residue is taken up with a small volume of hot water, 10 c.c. of concentrated hydrochloric acid are added and the solution is again evaporated to dryness. The residue is taken up with hot water and platinic chloride solution is added. When the solution is almost evaporated to dryness the dish is preferably taken off the water bath and twirled round so as to cover the dried portion with the liquid portion and so avoid a baked condition. The precipitate is covered with acidulated alcohol as previously described (*loc. cit.*) and allowed to stand for about an hour, the precipitate being thoroughly broken up. The precipitate is collected on a tared filter, washed with acidulated alcohol until the runnings are colourless, and then at least seven times with 10 c.c. portions of Lindo's ammonium chloride wash. The washing is continued five times with 80 per cent. alcohol, washing to the top of the funnels. The method has been tested in the presence of ammonium salts greatly in excess of the quantity likely to exist in commercial samples. It has also been tested in the presence of sodium nitrate, phosphatic matter and organic matter (cottonseed meal), and the results recorded are entirely satisfactory. J. F. B.

Method for Bringing Elementary Sulphur into Solution for Analysis. A. P. Bjerregaard. (*J. Ind. and Eng. Chem.*, 1919, 11, 1055.)—Most samples of sulphur leave a considerable residue insoluble in carbon bisulphide, and boiling with

nitric acid and bromine leads to the formation of fused globules difficult to attack, while bromine water causes the evolution of sulphurous gas. The procedure recommended by the author takes advantage of the solubility of sulphur in dry liquid bromine, the solution then being oxidised by concentrated nitric acid. About 0.1 grm. of sulphur is dissolved in 1 c.c. of bromine, and 10 c.c. of nitric acid are added. After removing the excess of bromine and nitrous fumes by heat, 100 c.c. of water and a few c.c. of hydrochloric acid are added and the solution is again boiled to expel the nitric acid. The sulphuric acid formed is then precipitated in the hot solution by barium chloride in the usual manner.

J. F. B.

Estimation of Zirconium by the Phosphate Method. G. E. F. Lundell and H. B. Knowles. (*J. Amer. Chem. Soc.*, 1919, **41**, 1801-1808.)—An experimental study of the conditions necessary for the quantitative precipitation of zirconium as phosphate has shown that the separation is complete from cold or tepid solutions containing 2 to 20 per cent. by weight of sulphuric acid, provided that an excess of from 10 to 100 per cent. of the theoretical amount of diammonium phosphate be used for the precipitation. The hydrolysis which takes place when the zirconium phosphate is washed with water may be prevented by washing the precipitate with a cold 5 per cent. solution of ammonium nitrate. Ignition of the precipitate washed in this way yields zirconium pyrophosphate, the zirconium oxide (ZrO_2) factor for which is 0.4632, but the compound obtained by igniting the precipitate after washing with water is not constant in composition. Zirconium can be quantitatively separated from iron, aluminium, chromium, cerium, and thorium, by precipitation as phosphate from its solution in 20 per cent. (by weight) sulphuric acid, whilst a satisfactory separation from titanium can also be effected by adding sufficient hydrogen peroxide to keep the titanium in solution.

C. A. M.

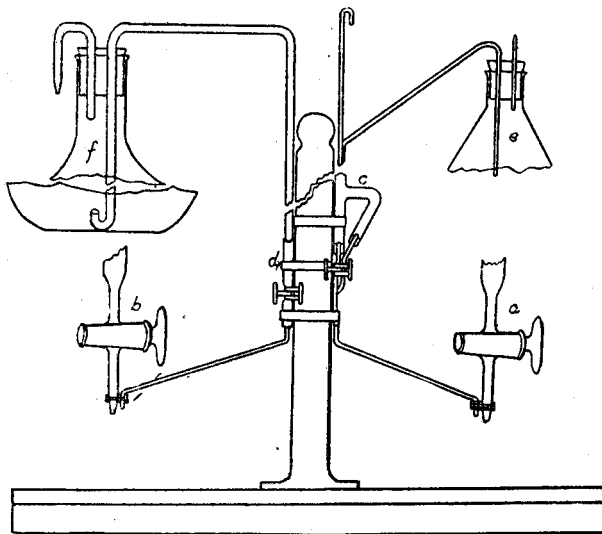
APPARATUS, ETC.

Determination of Ignition Temperatures by the Soap-Bubble Method. A. G. White and T. W. Price. (*J. Chem. Soc.*, 1919, **115** and **116**, 1248-1264.)—The soap-bubble method for the determination of ignition temperatures was first described by McDavid (*J. Chem. Soc.*, 1917, **111**, 1003), who obtained results in which the experimental error is assumed to be less than $\pm 3^\circ C$. His results are very high in comparison with other recent determinations. The authors have applied the method to determine the ignition temperatures of mixtures of ether, benzene, light petroleum, and hydrogen with air, and describe in great detail the conditions under which consistent results can be obtained. Even after careful standardisation of the coils used, size of bubble, and numerous other details, the results were found to be effected by the physical state of the igniting surface and the nature of the material of which it is made, alteration in the results obtained being observable even upon the addition of small quantities of the salts used for standardisation purposes, thus discrediting the method as one capable of giving the true ignition temperature of a gas mixture. The ignition temperature of a particular gas mixture

as determined by two different coils often varied by more than 150° C., and results indicated the unreliability of the method even for comparative purposes.

H. F. E. H.

Apparatus for Rapid Gastric Analysis together with a Method for the Preservation of Starch Solution. R. J. Miller. (*J. Ind. and Eng. Chem.*, 1919, 11, 963-964.)—In gastric analysis the following estimations are required at frequent intervals: Total acidity—titration with $\frac{N}{100}$ potassium hydroxide. Free acidity (Sahli method)—titration with $\frac{N}{100}$ sodium thiosulphate, finishing with starch solution. Formol titration or amino-acid—titration with $\frac{N}{100}$ potassium hydroxide after the addition of neutral formalin. The arrangement of apparatus illustrated in the figure has been devised as a permanent equipment for making these tests. The installation consists of two standard burettes of 30 c.c. graduated to 0.05 c.c., the burette, *a*, on the right being connected with the reservoir of standard alkali, and that on the left, *b*, with the thiosulphate. The burettes are fitted with a device for



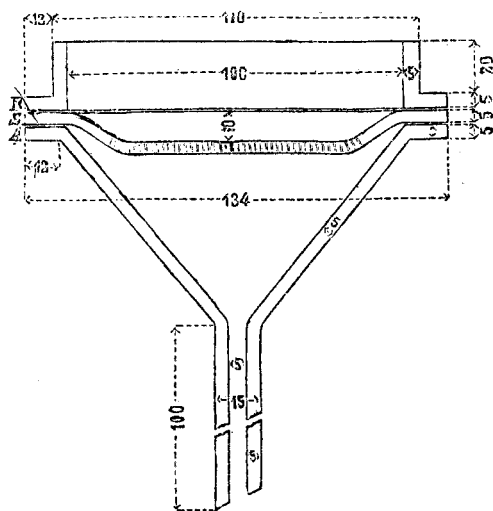
automatic filling to the zero mark when suction is applied to a branch tube. Attached to the upright portion of the burette-stand, by means of adhesive tape, is an automatic pipette, *c*, connected with the formalin reservoir, *e*, the pipette being controlled by a two-way pinchcock arranged so that as soon as the charge of formalin is delivered through the discharge-pipe leading to the point of the burette, *a*, the pipette automatically fills up again from the reservoir to its predetermined level and is ready for the next discharge. The attachment shown at *d* is also bound to the upright by tape, and is an ordinary siphon controlled by a pinchcock and connected with the reservoir, *f*, for starch solution, which is delivered as required to the point of the thiosulphate burette, *b*. For the preparation of a stable solution of soluble starch, 10 grms. of soluble starch are ground to a paste with cold water and added

to 750 c.c. of water which has been boiling for fifteen minutes. The mixture is heated for ten minutes and diluted with boiling water to 1 litre. The storage reservoir is rinsed with boiling water and the starch solution added, being immediately covered with a layer of $\frac{1}{4}$ inch of liquid paraffin. If desired, the hot starch may previously be shaken with 1 c.c. of toluene. The siphon is charged while the solution is still hot, and the reservoir is preserved in a sterile condition.

J. F. B.

Chemical Analysis with Membrane Filters. R. Zsigmondy and G. Jander.

(*Zeits. anal. Chem.* 1919, 58, 241-280.)—As a development of the collodion film ultra-filter, the authors have introduced a parchment-like membrane which has the appearance of glazed paper or white glacé kid, and which is prepared by the

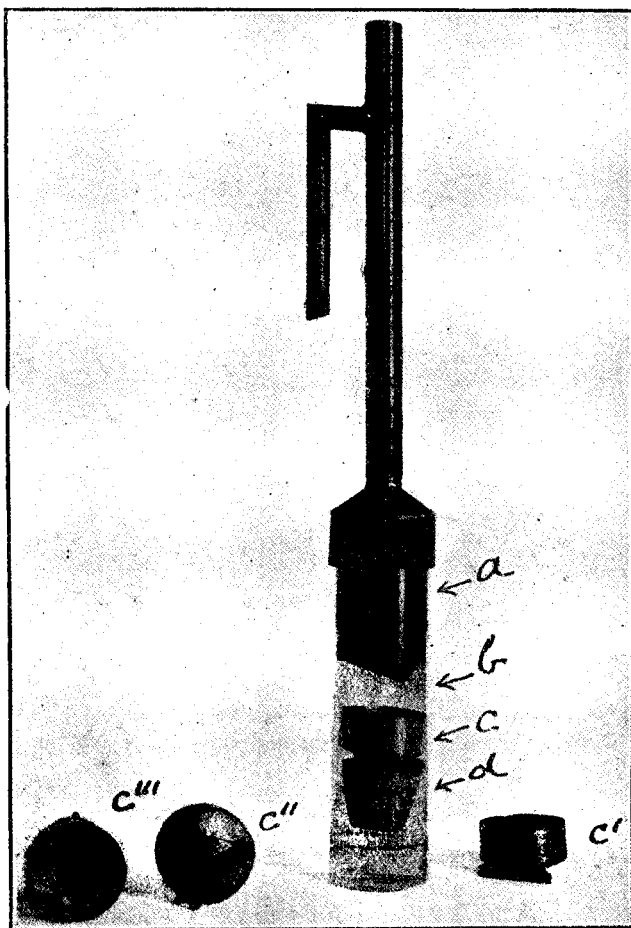


evaporation, under special conditions, of somewhat complex solutions of certain colloids. These filters, under the action of the suction pump, are permeable to water with a wide range of rapidity, but possess the property of retaining the finest and most gelatinous precipitates, and will even filter out colloidal suspensions of graphite, the filtered residue being readily and completely removable from the glazed surface. The membrane filters are used for all kinds of filtration in quantitative work in conjunction with an apparatus (see Fig.) resembling the Buchner funnel with a dished filter-plate. The funnel is made in three pieces which are held together by

screw clamps and with rubber rings between the parts. A smaller funnel has been designed to take the place of the Gooch crucible, and has a filter-plate of watch-glass shape representing a segment of a sphere. The filtering membranes are classified according to the rate of passage of 100 c.c. of water through a circular area of 100 mm. diameter, and the most useful kind for quantitative work ranges from twenty to fifty seconds. In using the filter the liquid is decanted at a uniform rate into the middle of the hollow, but must never come within 0.5 cm. of the joint. The precipitate is then brought on to the filter and drained by suction, and it is to be noted that, whereas the precipitate must be well drained, it must not be sucked so dry that cracks appear in the cake. These filters differ from paper filters in that none of the finer particles penetrate into the pores, but all remain free on the glazed surface. Filtration is facilitated if a paper filter be fitted against the plate immediately beneath the membrane. It is not desirable either to dry the membrane filter in the oven or to incinerate it; the best procedure is to remove the precipitate quantitatively into a crucible. This may be done either immediately in the wet condition or after drying in a suitable manner. Precipitates which dry to a loose powder are best handled moist. For this purpose the screw clamps are

loosened and the membrane is removed, bent round in the form of a scoop, and the main portion of the precipitate is pushed into the crucible with a horn spatula. The filter is then spread out over a deep crystallising dish, and the residue of precipitate washed down with a few drops of water and a small paint-brush into the hollow thus formed. The fluid is tipped into the crucible, and the last traces of precipitate are removed from the spatula and brush in a similar manner. The water is evaporated from the crucible on a water bath. In the case of gelatinous precipitates, the whole filter should be dried in the oven at 80° C. until the precipitate is partially dry but still semi-coherent. In this case the membrane must be kept under tension during drying, substituting rings of paper for the rubber-packing rings. J. F. B.

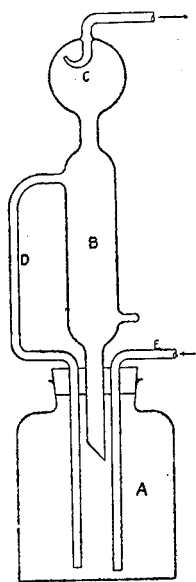
Fat Extraction Apparatus. J. M. Pickel. (*J. Ind. and Eng. Chem.*, 1919, 11, 1053-1055).—The author has devised a form of extraction apparatus with which



twenty analyses may be conducted simultaneously on an electric hot plate, $4\frac{1}{2}$ ins. \times 24 ins. About 15 c.c. of ether are used, of which one-third to one-half is

recovered. The change from extraction to recovery is effected by merely giving the condenser a slight turn on its axis. This condenser is made of metal, with cold water inlet extending down the centre, and the outlet passing up around it to an overflow discharging into a trough. The extraction is carried out in a cylindrical glass jar, *b*, $5\frac{1}{2}$ ins. high and $1\frac{9}{16}$ ins. in diameter inside. This is just sufficient to take the body of the condenser, which measures $1\frac{1}{2}$ ins. outside at the part marked *a*. The lower portion of the condenser, on which the condensation takes place, is narrowed down to $1\frac{7}{16}$, and the lower surface is tapered to an eccentric apex, or drip point, from which the condensed ether falls into the cup, *c*. This cup contains a funnel leading right through it, so that when the condenser is so arranged that the ether drips into the funnel, it passes through into the crucible beneath, whilst, if the condenser is turned so that the drip misses the funnel, the ether is collected in the cup and is recovered when the cup is removed. The cup and funnel are made of metal. The substance to be extracted is contained in the crucible, *d*, of alundum, and the drip of ether is distributed by placing a sheet of paper or perforated metal over the substance. The crucible is supported by lugs extending from the side of the glass cylinder, and the fat extract falls through the crucible to the bottom of the cylinder. If desired, a receiver of aluminium may be fitted in the bottom of the glass cylinder to receive the ethereal extract, in which case the lugs are omitted, and the crucible is supported in the upper part of the receiver. J. F. B.

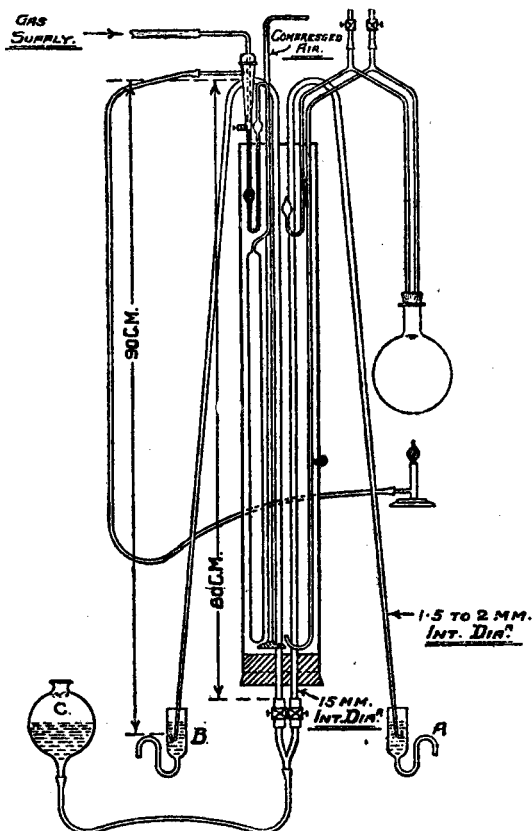
Nitrogen Generator for Laboratory Use. W. L. Badger. (*J. Ind. and Eng. Chem.*, 1919, 11, 1052-1053.)—The following description relates to a simplified



form of Van Brunt's apparatus for preparing nitrogen free from oxygen by the action of copper in the presence of an ammoniacal solution of an ammonium salt. A wide mouth bottle, *A* (see Fig.), is filled with the reagent and as much metallic copper as can be got into it, preferably in the form of straight vertical wires. *B* is a Liebig condenser shell with the lower water connection sealed up; it is filled with copper turnings or punchings. A tube, *D*, is connected to the upper water connection, and extends nearly to the bottom of the bottle, *A*. At the upper end of the condenser should be a bulb, *C*, although the trap as shown is not absolutely necessary. The gas inlet tube, *E*, should also reach nearly to the bottom of the bottle. A fourth tube may be added for blowing out spent reagent if desired. The bottle should hold 2 litres of reagent. This reagent is made by diluting 1 part of commercial ammonia with 1 part of water, and saturating the mixture with ammonium chloride. This reagent remains active until such a heavy precipitate is formed that the apparatus is clogged. A slow circulation of liquid takes place through the tube, *D*, and prevents premature clogging of the tower. The tower is preferably charged with 5 inches of copper punchings, which present a much larger

surface than turnings. Air or 95 per cent. commercial nitrogen is passed through the apparatus in a steady stream, and the ammonia carried over is absorbed in Drechsel washing bottles. J. F. B.

Apparatus for the Estimation of Vapour Pressures. A. Morton. (*J. Soc. Chem. Ind.*, 1919, **38**, 363-364r.)—The apparatus shown in the diagram is constructed without stopcocks, thus obviating errors caused by organic solvents dissolving the lubricants used for the taps. Two capillary tubes are fused to the top of the barometer tubes, and bent downwards so that their ends dip into the mercury reservoirs A and B. After the mercury in the apparatus has been dried with strong sulphuric acid the excess of the latter is forced from the barometer tubes into A and



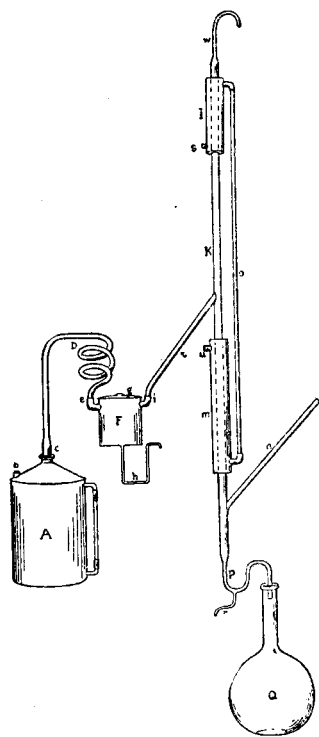
B by raising the reservoir C, and removed from A and B by means of a pipette and filter-paper. This treatment with acid is repeated until the mercury is at the same level in both tubes, and the distance between this level and that of the mercury in the reservoirs is equal to the barometric level at the time of the experiment. The liquid under examination is introduced into A, the screw clip on the left-hand tube closed, A lowered until the end of the capillary is immersed only in the liquid, and a sufficient quantity of the latter drawn up into the barometer tube by first raising and then lowering C, after which A is raised again so that the end of the capillary tube is again immersed in the mercury. The reservoir C is then lowered below the level of A, so as to keep the liquid in the barometer tube under reduced pressure, and the apparatus is kept at a constant temperature by means of a water-

jacket provided with a thermo-regulator and constantly stirred by means of compressed air. Bubbles of air escaping from the liquid are forced back into A by raising C and escape through the mercury seal. The reservoir C is again lowered, the left-hand clip opened, and the difference between the levels in the two tubes is measured with a cathetometer. After lowering C still further, the difference in the levels is again measured, and if the readings do not agree the vapour and air in the liquid under examination are forced back into A again, and this treatment is repeated until concordant results are obtained at different levels.

C. A. M.

Method for the Preparation of Conductivity Water. C. B. Clevenger.

(*J. Ind. and Eng. Chem.* 1919, 11, 964-966.)—The apparatus illustrated in the figure is a modification of the Bourdillon still, in which the steam is purified by means of



a current of pure air. The boiler, A, of about 15 litres capacity, is connected with the block-tin spiral D and the trap F, in which the spray and less volatile impurities are collected and discharged through h. The $\frac{3}{4}$ -inch tube, e, extends to within $\frac{1}{2}$ inch from the bottom of the trap, and the steam emerges from i, passing through the pipe, t, into the upright condenser, K, which is a block-tin pipe $1\frac{1}{4}$ inches in diameter, and 6 feet long. Copper cooling jackets, l and m, are connected together by the glass tube, o. The container, q, of glass or block-tin, is attached to the syphon, P, by a rubber stopper; a syphon or water-tap is provided for drawing off the water, and a guard-tube of soda lime to purify the air which enters. The outlet, r, closed by a tin stopper, is used for drawing small samples for testing. The main air stream enters through a purifying system attached to n, and is preferably produced by means of a small rotary pump. The air is purified by passing through two large bottles containing sulphuric acid and broken glass, and two similar bottles containing concentrated sodium hydroxide solution; afterwards it passes through a vertical column of glass beads, and, finally, through an empty bottle serving as a trap. The tube, w, at the top of the condenser, is also provided with a train of guard bottles, to prevent

access of carbon dioxide and ammonia. In operation, the water in the still is first boiled for a short time to expel gases, and then a few c.c. of phosphoric acid are added. About one-fourth of the steam condenses in the trap and carries away impurities. The steam entering K is purified by the upward air-stream, and is cooled just to condensation by the upper jacket, l. As the hot water runs down the sides of K, it continually meets air, which is less and less contaminated, and is finally cooled by the lower jacket, m. The speed of the air current is only limited by the efficiency of the purification apparatus, and the air escaping at w carries away the volatile

impurities of the water. All parts which are in contact with steam are either of block-tin or tin-lined; permanent connections are soldered, but movable connections are luted with tin-foil. The output of the still is about 1 litre per hour of water, having a conductivity value of 0.8×10^{-6} reciprocal ohms. J. F. B.



REVIEWS.

CHEMICAL REAGENTS: THEIR USES, METHODS OF TESTING FOR PURITY AND COMMERCIAL VARIETIES. By DR. C. KRAUCH, Chemist to the Firm of E. Merck, Darmstadt. Second English Edition, Revised and Enlarged by H. B. STOCKS, F.I.C. Pp. vi + 368. London: Scott, Greenwood and Son, 1919. Price 17s. 6d. net.

A good selection of reagents is considered in this book. Of course, no one will find it covers their every need, but those excluded are reagents of secondary importance. Thus among omissions are *o*-tolidine, silver lactate, sodium citrate, aluminium chloride, mannitol, cadmium sulphate, and Sudan III.

While dealing with the detection of, and proposing limits for, impurities, the work is very methodical and quite good. There is some cold-blooded restraint, which is probably intentional; for a liturgy on the catastrophes that will arise from, say, ammonia in sulphuric acid, lead and iron in zinc, carbonate in ammonium hydroxide, and oxidisable matter in acetic acid, would be quite easy to begin, but it would be without end. On this, the main purpose of the book, comments of a trivial order only are called for. As a limit of acidity in 40 per cent. formaldehyde, 1 c.c. is required to show no acid reaction after adding one drop of normal alkali. This is liberal, because the reviewer has never met a batch requiring half as much alkali. Not one in ten samples of the cream of tartar met with in this country will, after the addition of ammonia, give no colour with hydrogen sulphide.

Under paragraph headings of "Commercial Varieties," the names and composition of chemicals of inferior quality are given, which adds to the usefulness of the book.

It is evident that only the laboratory worker is considered, as the uses of a substance in the arts and technical processes are seldom mentioned. The general plan for "Uses" is this: The reader is told that a substance is used for one purpose, and referred to a published paper; and for another purpose, and referred to a text-book. The full scope of a reagent is often not fully recognised; and even where references or descriptions of tests are given, they are not indexed. Thus, at least two tests for furfural are mentioned, one of which is also described. Neither is indexed, and, to find them, one must search till they are found in monographs devoted to sulphuric acid and xylydine respectively.

Glycerol is regarded solely as a boric acid reagent, alkanet only as an indicator, picric acid is confined to alkaloid, albumin and naphthalene reactions, and the uses

of benidine in food analysis and enzyme work are omitted. The last is regarded solely as a sulphuric acid and a blood reagent. It is probably not often used now for the latter purpose, except for occult blood in fæces.

Starch is the only substance with which a simple iodine solution is said to give a colour. Formaldehyde is regarded solely as an antiseptic; without agreeing entirely with some optimists among American physiological chemists that distillation in Kjeldahl's process can be avoided by the use of formaldehyde (the reviewer's experience is that results on the low side are usually obtained), there are nevertheless several conditions when the attraction of amino groups and ammonia for it may be utilised. There are the "aldehyde figure" for proteins, Sorensen's method for amino-acids, E. W. Brown's method for ammonia in urine, and it has also been recommended by Krapivini for the estimation of ammonia in effluents and sewage. The suitability of iron alum for salicylic acid is not mentioned, and ferrous sulphate is only a nitrate-test reagent.

Actual errors are few and include a statement that the stain produced on mercuric chloride paper by arseniuretted hydrogen is unaffected by light or moisture, and the necessity of drying turmeric paper to bring out the red due to boric acid is overlooked. It is not meticulous accuracy to say all salts of barium are poisonous, as five ounces of the sulphate are given as a radiographic meal.

Methyl violet is selected for the detection of mineral acid in vinegar, and tropæolin 00 paper for hydrochloric acid in gastric juice, but there is no direction to warm the test-paper in the latter case to reveal small amounts. There is no mention of dimethyl-amino-azo-benzene, which is the most popular indicator for estimating hydrochloric acid in gastric contents. In a recognition of the work of Lubs and Clark, phenol-red is mentioned. This is the indicator which has quite recently been adopted by the Medical Research Committee, National Health Insurance, for the hydrogen ion concentration of bacteriological media.

The references to "Commercial Organic Analysis" are to editions published during Mr. Allen's lifetime; there is a reference to the second edition of Clowes and Coleman's "Quantitative Analysis"; and there are only five references to papers in all the last twenty volumes of the ANALYST.

A Tralles alcohol table is provided. Tralles got his order for this article from the Prussian Government in 1811, since when a gravity lower than 0.7946 at 60° F. has been found and accepted for 100 per cent. alcohol. A reader desiring an interpolated table is referred to Hehner's tables in Muspratt's "Handbuch der technischen Chemie." These tables were published in Vol. V. of the ANALYST, and subsequently reprinted in pamphlet form by J. and A. Churchill. There is no reference to Thorpe's compilation of 1916.

If the reviewer has read correctly between the lines of the Preface, no foreign assistance has been invoked since the publication of the former edition in 1902.

WILLIAM PARTRIDGE.

THE CHEMIST'S YEAR-BOOK, 1918-19. Edited by F. W. ATACK. Fourth Edition.

Two vols., pp. 1146. Sherratt and Hughes, Manchester. Price 15s. net.

The fourth edition of this admirable reference book has made its appearance (previous editions havin been reviewed in this Journal: see ANALYST, 1915, 40, 427; 1917, 42, 406), and the editor and contributors are to be congratulated upon their success in the production of such an invaluable *vade-mecum*, which continues to receive further useful additions with each succeeding edition. The new sections added to the present volumes include "Analysis of Clays, Firebricks, and Silica Materials," by J. W. Mellor; "Agricultural Chemistry," by E. J. Russell; and "Crystallography," by E. H. Rodd; while several of the older sections have been revised, and the tables giving the properties of inorganic and organic substances have been entirely reset, with a decided increase in utility.

The annual revision to which this work is subjected still leaves some matters of minor importance outstanding. Considering the value in many industries of the estimation of arsenic in various materials, it is to be expected that one at least of the principal methods employed should be given in some detail, but the reviewer has failed to discover any reference whatever throughout the volumes. Further omissions, which might readily be rectified, occur in the table "General Properties of Organic Compounds," from which the densities of various common substances, such as trichlorethylene, vanillin, phenolphthalein, etc., are missing.

A few of the tables, although correctly indexed, are misplaced; for example, the "Solubilities of Bromine" on p. 540 appear in the section devoted to the solubilities of gases in liquids, while the "Solubility of Ether" occurs on p. 555 under the heading "Solubilities of Solids in Liquids." These two tables, together with the "Solubility of Aniline" on p. 973, might be included in a small section by themselves. The Temperature Conversion table—Centigrade to Fahrenheit—on p. 420 should immediately follow the corresponding table on p. 418. In the table "General Properties of Inorganic Substances," pp. 142-208, the editor has followed the usual unsatisfactory plan of expressing solubility by the terms "soluble," "slightly soluble," etc. The futility of this method may readily be demonstrated by requesting several chemists to express their numerical conceptions of these terms, when the results will be found extremely variable. Some endeavour should be made to give approximate values, or else definite limits should be given to the above terms. The contraction "diss.," which occurs occasionally in the last column of the above tables, will present no difficulty to the trained chemist; but for the benefit of the many other users of this book, the definition of this contraction should be provided at the bottom of p. 142.

Some of the tables will not meet with the use their importance deserves, for the reason that no references to them are given in the index. Among these are the pressure conversion table on p. 408, the "Delicacy of Certain (Alkaloid) Precipitating Reagents," p. 1049, and the "Boiling-Points of Glycerine Solutions" on p. 613. The latter is certainly included under the index title of "Glycerine Solutions: Vapour Pressure of," but no indication is given that the boiling-points are also furnished. There is no apparent reason why the two tables giving the boiling-points of alcohol solutions on pp. 619 and 939 should be indexed, the one under the

letter "A" and the other under "E" (Ethyl Alcohol). Both should obviously appear under the heading of Alcohol.'

The book is almost free from serious errors, but the following should be rectified: On p. 383 the table "Measures of Capacity" (B.P., 1914) gives a centilitre (Cl.) as equivalent to 0.01 c.c. (0.169 minims), and 1 decilitre (Dl.) equal to 0.1 c.c. (1.69 minims). In earlier editions of the book these equivalents are given correctly, but in slightly different form, and the error has evidently crept in during transcription. The table on p. 441, giving the specific gravity of acetic acid solutions, still retains the inaccurate figure of 1.0007 for the sp. gr. of a 1 per cent. solution, but for this error the author of the table and not the editor is to be held responsible. However, in spite of the above faults, the book is of great value, and very well worth the price charged. Now that the diary of doubtful utility has been omitted, a few blank pages might be inserted at the end of Vol. II. for users to note down any corrections or suggestions which might be of service to the editor when preparing the next edition, together with a date before which such communications should be sent in.

T. J. WARD.

GAS AND FUEL ANALYSIS FOR ENGINEERS. By AUGUSTUS H. GILL. 1919. John Wiley and Sons; London: Chapman and Hall. Price 6s. net.

The author claims that his book "is an attempt to present in a concise, yet clear, form the methods of gas and fuel analysis in testing the efficiency of a boiler plant." The first chapters are devoted to apparatus and methods employed in simple flue gas analysis, and to temperature measurement—the latter a short chapter of less than three pages, which is unlikely to be of much service to anyone, so "concise" is it. Chapter V. deals with gas analysis with the Hempel apparatus. A brief description is given in the succeeding chapters to solid, liquid, and gaseous fuels. Evidently American practice with gaseous fuels is different in some respects from ours, for we learn that "coal or illuminating gas was formerly produced by the distillation of bituminous coal; it is at present made by the enrichment of water-gas."

Methods for the analysis of fuels and calorimetry follow, the Emerson type of bomb calorimeter (a form practically unknown in this country) being selected. The method described of taking half the loss by radiation per minute as the basis for the cooling correction is unsatisfactory for a calorimeter capable of a considerable degree of accuracy. In connection with calorimetry it is surprising to find the author describing the quite discredited Berthier method (estimation of calorific value by the weight of lead reduced from litharge) and even referring to it as a "method which would seem worthy of more attention than it has received."

In discussing the calorimetry of gases it is stated that "the net heating value of a gaseous fuel represents the conditions in which by far the greater quantity of gas is consumed for cooking, heating, and gas engines, and is the one which should be reported." Possibly the author is unaware of the different and more scientific attitude adopted to-day in reference to gross and net calorific values, an attitude so well summarised by one authority as "the figure obtained by subtracting the heat due to condensation of the water was absolutely artificial and meant nothing."

The author in attempting conciseness has frequently succeeded in producing

“scrappiness.” His working directions would frequently require amplification by a good teacher. The appendix contains some useful tables and specifications for coal and oil purchase.

J. S. S. BRAME.

THE ANALYSIS OF MINERALS AND ORES OF THE RARER ELEMENTS. By W. R. SCHOELLER, Ph.D., and A. R. POWELL. Pp. x+240. London: Charles Griffin and Co., Ltd. 1919. Price 16s. net.

On its title-page this book is described as for analytical chemists, metallurgists, and advanced students, and in the preface the authors say that the old arbitrary separation into common and rare elements is still adhered to by most teachers, with the result that the training of the future chemist can hardly be said adequately to prepare him for present-day requirements. It might be argued that the student would prepare himself better for his life's work, whatever it may be, by attempting to master the foundations of analytical chemistry rather than by studying methods for the separation of comparatively rare elements. If he has done that, he will have no difficulty in making use of this book or a later edition of it, if and when he is called upon to estimate one of the rarer elements. To the older professional man it would be difficult to exaggerate the value of this book. Half of us may go through our professional life without once being called upon to look for or to estimate a rare element; to a few a single group of rare elements may be as familiar as iron or carbon to the rest of us, but half of us have no such special interest, and yet may be called on to estimate rare elements as an unusual development of our ordinary work. The preliminary hunt through the literature is rendered easier than was formerly the case by the well-indexed volumes of the ANALYST, but is still tedious and often unprofitable unless the analyst has ready access to a good library or is the owner of an exceptional one.

It would be difficult to embark on a critical review of a book of this scope. Three-quarters of the separations described the reviewer has never attempted; many of the remainder but once or twice. A close study of the pages he would feel confidence in criticising revealed nothing conflicting with his own experience, and will encourage him to refer to other sections of the book with confidence. No doubt some indifferent methods have been included; the authors frankly state that in such a book a certain amount of compilation is unavoidable, and that no chemist has opportunity to test all the methods covering so vast a subject. It is to be hoped that other chemists will not only refer to this book for information, but will read critically those sections which they could write themselves, and that they will find time to point out any errors to the authors; for this is a book of which a new edition will be called for every five years, supposing analytical chemistry maintains the rate of progress which marked the five years ending with 1914. And, in any new edition, one may be permitted to express the hope that for every new method included one old one may be dropped. The fact that this book is so small is one of its merits. If and when it gets to twice the size, it will probably be a worse book. It has been said that it takes ten years for a new method to get into the textbooks and twenty years for a bad one to drop out. This book contains methods described only last year, and there are signs that the authors wished to avoid the reproach of

offering a bewildering choice of alternative methods. If they maintain this attitude in future editions, and ruthlessly scrap third-best methods, the path of the next generation of analytical chemists will be smoothed.

It has been taken for granted that every chemist at all likely to be called upon to estimate unfamiliar elements—and that is half the readers of the *ANALYST*—will acquire this book, and so no detailed statement of its scope has been given. The title gives almost all the information required as to the scope of the work, but perhaps it should be added that it deals with lithium, titanium, vanadium, selenium, tellurium, molybdenum, tungsten, uranium, and the platinum metals, as well as with the still rarer elements.

G. C. JONES.

VOLUMETRIC ANALYSIS. Second Edition. By C. H. HAMPSHIRE, B.Sc. (Lond.), F.I.C. Pp. 127. 1919. London: J. and A. Churchill. Price 5s. net.

In the second edition of this little volume newer matter has been added in order to meet requirements of the British Pharmacopœia, and, although primarily written for pharmaceutical students, the contents deal with general volumetric analysis and should be useful to all young students of chemistry. The chapter on "Indicators" might with advantage be supplemented and strengthened by a summarised table, and, in dealing with examples from organic chemistry where only in some cases are molecular and constitutional formulæ given, an extension of this feature would have been more consistent.

The application of normal solutions is well expressed, and repetition of calculations is designed to compel a clear understanding of fundamental principles.

The chapters assigned to acidimetry and alkalimetry, oxidation and reduction, are exceedingly well written and free from error, and throughout the book the influence of conditions is well stressed.

More advanced students will observe omission of details underlying principles in some of the methods, notably oxidation of formaldehyde by iodine, but, having regard to the preface, serious exception cannot be taken to this, and the volume can be regarded as having fulfilled the author's claim. It is a useful little handbook.

GEO. R. THOMPSON.