

THE ANALYST.

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

ORDINARY MEETING, JUNE 4, 1919.

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

Certificates were read for the first time in favour of Capt. John Dalton.

Certificates were read for the second time in favour of Messrs. Andrew More, F.I.C., John Haworth, F.I.C., and Henry Turner Lee, M.Sc., A.I.C.

The following were elected Members of the Society: Messrs. Charles Frederick Lee Barber, A.I.C., George Stanley Withers Marlow, B.Sc., F.I.C., Frederick William Read.

The following papers were read: "Examination of Commercial Samples of Nicotine," by Percival J. Fryer, F.I.C.; "Mexican Insects in Poultry Food (*Notonecta*, *Corixa* and Mexican Cantharides)," by T. E. Wallis, B.Sc., F.I.C.; "A Rapid Method for determining Nickel and Cobalt in Ores and Alloys: Part III.," by W. R. Schoeller, Ph.D., and A. R. Powell; "Note on the Oil of *Ceratotheca sesamoides*," by E. Richards Bolton, F.I.C.; "An Improved Method for the Estimation of Nitrates in Water by Means of the Phenolsulphonic Acid Reaction," by Robert C. Frederick; "Estimation of Morphine in Indian Opium," by Jitendra Nath Rakshit, and Frank J. D'Costa.



A METHOD FOR THE DETERMINATION OF MONOCHLORBENZENE IN MIXTURES CONTAINING BENZENE, MONOCHLORBENZENE AND DICHLORBENZENE.

BY N. G. S. COPPIN, M.Sc., A.I.C., AND F. HOLT, O.B.E., M.Sc., A.I.C.

(*Read at the Meeting, April 2, 1919.*)

THE authors, who for some time past have been engaged in the manufacture of monochlorbenzene, have found the need of a method for estimating the quantity of this substance in crude chlorinated benzene, and in mixtures obtained during the distillation of the crude product.

After a number of attempts to devise methods based upon fractional distillation and specific gravity, it was found that the best results were obtained from determinations carried out on similar lines to D. Northall-Laurie's "New Method for the Determination of Toluene in Commercial Toluols" (*ANALYST*, 1915, **40**, 384). At the outset the authors desire to express their indebtedness to Mr. D. Northall-Laurie for his kindness in allowing them to make use of his method for this purpose, and to publish it.

The method consists in distilling at a uniform rate a known volume of the sample to be tested, from an ordinary distilling flask, into an efficient condenser. One quarter of the original volume is collected; the receiver is then changed and a further half distilled over. The distillation is then stopped, leaving the remaining quarter in the flask. The boiling-points of the first fraction collected, and the residue in the flask, are then determined in a specially designed apparatus. From these boiling-points, by reference to a graph drawn up from the results of determinations made with known mixtures, the composition of the sample in question can be read off. The theoretical principles underlying this method are fully discussed in the paper quoted above, and need not be repeated here.

In drawing up the graph for monochlorbenzene, mixtures of benzene, monochlorbenzene and *p*-dichlorbenzene, of known composition *by weight*, were prepared from specially purified substances. It is necessary to determine the composition by weight instead of by volume, owing to the fact that the third constituent, *p*-dichlorbenzene, is a solid. Determination by weight is an advantage when applied to commercial work, since the chlorine derivatives of benzene are sold by weight.

In the chlorination of benzene a small quantity of *o*-dichlorbenzene is formed along with the *p*-isomer; but as the boiling-points of these two substances only differ by 7° C., and as the *p*-body greatly predominates in the dichlorbenzene mixture, the error in the boiling-point, due to using *p*-dichlorbenzene alone in the determinations, is so small as to be practically negligible.

Further, a very small quantity of trichlorbenzene is present in crude monochlorbenzene, but this has not been taken into account in working out this method of analysis, as the amount is too small to affect the results to any appreciable extent.

Method.—The sample to be tested must first be carefully dried, as the presence of a trace of moisture renders the determination unreliable. Anhydrous calcium

chloride may be used for this purpose, but the authors find that sodium peroxide is by far the best drying agent for chlorinated benzene. Two hundred c.c. of the dried sample are placed in an ordinary distilling flask of suitable capacity, surrounded by a wire gauze cylinder to protect from currents of air, and the contents distilled, at a uniform rate of 7 c.c. per minute, through a Liebig condenser (30 inches in length) into a 50 c.c. measuring cylinder. When 50 c.c. have been collected, the cylinder is quickly replaced by a 100 c.c. cylinder, without interrupting the distillation. When 98.5 c.c. have come over into the second cylinder, the flame is extinguished, and the contents of the flask allowed to cool. In this way 100 c.c. are collected after the condenser tube has drained.

The contents of the 50 c.c. cylinder, and the residual 50 c.c. in the distilling flask, are transferred to two special constant boiling-point flasks, described in Northall-Laurie's paper (*loc. cit.*).

Each of these flasks is fitted with a thermometer, graduated so that the boiling-point can be accurately read to one-tenth of a degree. These thermometers should previously be calibrated against a standard thermometer, or by means of pure liquids of known boiling-point.

The outlet neck of each flask is connected with a reflux condenser. The authors find one of Cribb's pattern is very suitable for this purpose. The flask rests in a hole $1\frac{1}{4}$ inches diameter cut in a square of asbestos board. This board forms the top of an asbestos box, in which is enclosed the Bunsen burner, the top of which is $1\frac{3}{4}$ inches below the flask. The flask itself is protected from draughts by means of a cylinder of wire gauze, and the thermometer stem is protected from convection currents by a square of asbestos or cardboard slipped over the thermometer and resting on the cork. A second thermometer is suspended by the first in order to give the temperature of the surrounding air, which is required for making the stem-correction.

The rate of boiling is regulated so that the distillate falling back from the reflux condenser does so at the uniform rate of one drop per second. A stop-watch was employed for checking this rate in making the determinations for the graph. The supply of gas to the burners was regulated by a specially constructed tap, as shown in the accompanying sketch (see next page).

After ten minutes' boiling, the temperature should be constant; the thermometer is then read, and the necessary corrections made for atmospheric pressure and for the unheated portion of the thermometer. Details of these corrections are given below.

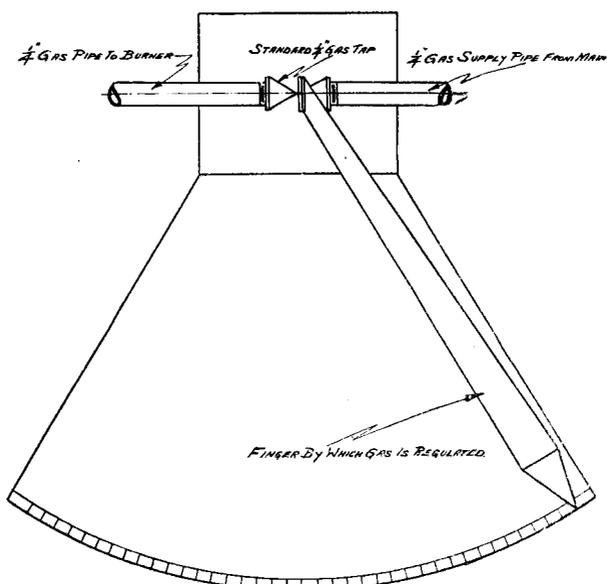
Determination of Results.—Having thus found the boiling-point of the first fraction and the residue, the percentages of benzene and monochlorobenzene are then read off from the graph, on which the boiling-points of the first 50 c.c. are plotted as ordinates against the boiling-points of the last 50 c.c. as abscissæ. The difference between the sum of the percentages of benzene and monochlorobenzene and a hundred represents the percentage of dichlorobenzene.

Precautions.—In samples containing more than 25 per cent. of dichlorobenzene care must be taken to prevent the solidification of this substance in the condenser towards the end of the distillation and on transferring the residue from the distilling flask to the boiling-point flask. Crystallisation in the condenser can be prevented

by circulating cooling water through the outer jacket while the first 50 c.c. come over, stopping the flow of water while the second 50 c.c. are distilled, and emptying the condenser during the distillation of the third 50 c.c. In order to prevent the formation of crystals during the transference of the residue, the empty boiling-point flask should be heated in a water-oven to a temperature above 53°C ., the melting-point of *p*-dichlorobenzene. The residue in the distilling flask is allowed to cool to a temperature of about 70°C ., and is then poured quickly into the hot boiling-point flask.

If these precautions are observed, all errors due to crystallisation can be avoided.

Note on the Graph.—The graph is divided up into longitudinal divisions representing the percentages of monochlorobenzene, and into lateral divisions representing



the percentages of benzene. It gives direct results for all possible mixtures of benzene, monochlorobenzene and *p*-dichlorobenzene, containing from 50 per cent. to 100 per cent. of monochlorobenzene.

The greater number of samples dealt with in commercial work contain from 0 to 30 per cent. of benzene, and in the section of the graph showing the composition of such mixtures each division represents a difference of 1 per cent. This enables the percentages to be read with an accuracy of 0.1 per cent.

In that section which shows the composition of mixtures containing from 30 per cent. to 50 per cent. of benzene the 1 per cent. divisions have not been drawn, in order to avoid a multiplicity of lines in a small space. Each division here represents a difference of 5 per cent.

When dealing with samples containing less than 50 per cent. of monochlorobenzene, it is necessary to add a known *weight* of pure monochlorobenzene, thus bringing the results on the graph. This can be done by weighing out 150 grms. of

the sample, adding to it 150 grms. of pure monochlorbenzene, and then distilling 200 c.c. of the mixture, afterwards correcting the results for the addition of monochlorbenzene.

Although it is not absolutely necessary, the authors find it advisable to adopt the above procedure in the case of all mixtures containing over 30 per cent. of benzene, to insure greater accuracy on the graph.

Boiling-Point Corrections.—The true boiling-point is obtained from the observed boiling-point by correcting for: (1) Variations in atmospheric pressure; (2) the portion of the thermometer stem which is not heated by the vapour of the boiling liquids.

1. The correction for atmospheric pressure is calculated from the following equation: $\Delta T = (760 - p)(273 + t)C$; where ΔT is the difference between the observed boiling-point and the boiling-point under 760 m.m. pressure, t is the observed boiling-point, p is the atmospheric pressure, and C is a constant. The value of C for benzene, monochlorbenzene and dichlorbenzene may be taken as 0.00012.

2. The correction to be added for the unheated portion of the thermometer calculated from the formula: $0.000143(T - t)N$; where T is the observed boiling-point, t the temperature of the stem outside the flask, and N the length of the mercury column in scale degrees which is unheated by the vapour. The necessary corrections should be calculated to the nearest 0.05°C .

Accuracy.—The graph has been checked by means of a large number of determinations using mixtures of known composition, and has been found to give results with an accuracy of 0.1 per cent.

The method affords a means for the rapid analysis of commercial chlorbenzenes, which are of increasing importance.

The authors wish to record their thanks to Miss M. Lunt and Mr. R. Thomas for their assistance in making the large number of determinations required for drawing up and checking the graph.

The above method is published with the kind permission of the Castner-Kellner Alkali Company, Ltd., in whose laboratories the work has been carried out.

RUNCORN, CHESHIRE.



THE COMPOSITION OF BUTTERMILK.

By T. R. HODGSON, M.A., F.I.C.

IN attempting to obtain some information with respect to the composition of buttermilk, the author was able to find only very few references; practically the only reference of any value was found in Richmond's Dairy Chemistry, which states that buttermilk "differs only slightly in composition from skimmed milk," the following analyses being given: Prepared from sour cream, fat 0.5 per cent., solids-not-fat 7.85 per cent.; prepared from milk, fat 0.5 per cent., solids-not-fat 8.37 per cent.; prepared from sweet cream, fat 0.35 per cent., solids-not-fat 8.67 per cent.; prepared

from separated milk, fat 0·1 per cent., solids-not-fat 8·93 per cent. ; Richmond also states that it is very rare to find as much as 2 per cent. of fat and also that it may contain water or other substances added during the churning.

Inasmuch as the above analyses differ very materially from those obtained in this laboratory, and as it is very important to the Public Analyst to know how much added water may be expected, the author thinks that it might be of interest to give the results obtained with samples of buttermilk taken for analysis under the Sale of Foods and Drugs Acts.

Buttermilk is a staple food in many parts of the country, and it is essential that the fraudulent addition of water should be prevented. It is well known that temperature has a very important influence on churning ; if the temperature is too high, the production of butter is retarded, while if it is too low, the solid butter grains enclose liquid fat, the best temperature being from 51° to 57° F. The inevitable result of this is that a certain amount of water is added in order to bring the temperature between those figures, and the vendor is therefore in a measure protected by Section (6) Sub-section (4) of the Sale of Foods and Drugs Act, 1875, which states that an offence shall not be deemed to have been committed "where the food is unavoidably mixed with some extraneous matter in the process of production." The problem which arises, is how much water may be said to have been unavoidably added during "the process of production" and how much has been added fraudulently.

There are no cases on record of any decision on the point having been given by the High Court either in England or Ireland, but the High Court of Justiciary in Scotland, in Warnock v. Johnstone, held that Sub-section (4) of Section (6) covered the defendant where 30 per cent. of water was added to the sample.

It has therefore been the practice in this laboratory to caution the vendors of samples containing over 25 per cent. of added water and less than 30 per cent., and to take legal proceedings in all cases where the added water exceeds 30 per cent.

The amount of fat present in the sample, of course, depends on the efficiency of the churning operations, but rarely exceeds 0·6 per cent. where the operation is carried on even approximately in an efficient manner.

TABLE A.

Percentage of Fat.	Number of Samples.	Percentage of the Whole.	Percentage of Fat.	Number of Samples.	Percentage of the Whole.
Under 0·1	Nil	—	0·9-0·99	6	1·9
0·1-0·19	5	1·6	1·0-1·09	2	0·6
0·2-0·29	15	4·8	1·1-1·19	2	0·6
0·3-0·39	61	19·6	1·2-1·29	Nil	—
0·4-0·49	81	25·9	1·3-1·39	1	0·3
0·5-0·59	64	20·5	1·4-1·49	1	0·3
0·6-0·69	33	10·6	1·5-1·59	2	0·6
0·7-0·79	20	6·4	1·6-1·69	1	0·3
0·8-0·89	16	5·1	1·7-1·79	2	0·6

TABLE B.

Solids-not-Fat.	Number of Samples.	Added Water.	Percentage of the Whole.
3·7-3·79	1	56·5-55·4	0·3
3·8-4·49	Nil	55·3-47·2	—
4·5-4·59	1	47·0-46·0	0·3
4·6-4·79	Nil	45·8-43·6	—
4·8-4·89	1	43·5-42·5	0·3
4·9-4·99	1	42·3-41·3	0·3
5·0-5·09	Nil	41·2-40·1	—
5·1-5·19	3	40·0-38·9	1·0
5·2-5·29	Nil	38·8-37·8	—
5·3-5·39	2	37·7-36·6	0·6
5·4-5·49	1	36·5-35·4	0·3
5·5-5·59	3	35·3-34·2	1·0
5·6-5·69	4	34·1-33·1	1·3
5·7-5·79	5	32·9-31·9	1·6
5·8-5·89	5	31·8-30·7	1·6
5·9-5·99	6	30·6-29·5	1·9
6·0-6·09	13	29·4-28·4	4·2
6·1-6·19	8	28·2-27·2	2·6
6·2-6·29	6	27·0-26·0	1·9
6·3-6·39	13	25·9-24·8	4·2
6·4-6·49	24	24·7-23·7	7·7
6·5-6·59	17	23·5-22·5	5·4
6·6-6·69	21	22·4-21·3	6·7
6·7-6·79	21	21·2-20·1	6·7
6·8-6·89	18	20·0-18·9	5·8
6·9-6·99	14	18·8-17·8	4·5
7·0-7·09	22	17·7-16·6	7·1
7·1-7·19	13	16·5-15·4	4·2
7·2-7·29	14	15·3-14·2	4·5
7·3-7·39	16	14·1-13·1	5·1
7·4-7·49	8	12·9-11·9	2·6
7·5-7·59	8	11·8-10·7	2·6
7·6-7·69	9	10·6-9·5	2·9
7·7-7·79	7	9·4-8·4	2·2
7·8-7·89	6	8·2-7·2	1·9
7·9-7·99	6	7·1-6·0	1·9
8·0-8·09	2	5·9-4·8	0·6
8·1-8·19	3	4·7-3·7	1·0
8·2-8·29	Nil	3·5-2·5	—
8·3-8·39	1	2·4-1·3	0·3
8·4-8·49	3	1·2-0·1	1·0
8·5 and over	6		1·9

The analyses given in the tables represent the results obtained on 312 samples, which were purchased in the ordinary course under the Sale of Foods and Drugs Acts; Table A shows the percentages of fat obtained, the highest being

1.7 per cent. and the lowest 0.1 per cent. ; it is noteworthy that over 25 per cent. of the samples contained less than 0.4 per cent., over 50 per cent. contained less than 0.5 per cent. and over 80 per cent. less than 0.7 per cent.

From the above results, it is obvious that where the fat exceeds 0.7 per cent., the process used must be inefficient and also that the fat under good conditions should not exceed 0.6 per cent.

Table B gives the percentages of solids-not-fat obtained on the same 312 samples, showing the corresponding percentages of added water, the lowest amount of solids-not-fat obtained was 3.71 corresponding to the presence of 56.4 per cent. of added water, while 6 of the samples contained 8.5 per cent. or over of solids-not-fat.

No less than 23 per cent. of the samples contained 25 per cent. or over of added water, while 8 per cent. contained over 30 per cent. ; in every case where more than 30 per cent. was present legal proceedings followed, and in practically every case the vendors were convicted and fined ; over 50 per cent. of the samples contained less than 20 per cent. of added water.

Table C shows the average solids-not-fat and the corresponding amount of added water for the samples received during each month of the year.

TABLE C.

Month.	Number of Samples.	Average Solids-not-Fat.	Added Water.
January	17	6.79	20.12
February	19	6.82	19.77
March	43	6.96	18.11
April	27	7.10	16.47
May	22	6.89	18.94
June	43	6.88	19.06
July	18	6.57	22.71
August	19	7.02	17.42
September	22	7.03	17.30
October	10	6.71	21.06
November	32	6.60	22.35
December	40	6.92	18.59

The highest average of solids-not-fat was obtained in April—namely, 7.10 per cent.—corresponding to 16.47 per cent. of added water, and the lowest in July of 6.57 per cent., corresponding to 22.7 per cent. of added water.

In Tables D and E are shown the monthly averages of solids-not-fat and the corresponding percentages of added water, when the samples containing 25 per cent. or over of added water in Table D and 20 per cent. or over in Table E are not taken into consideration.

TABLE D.

Month.	Solids-not-Fat.	Added Water.	Month.	Solids-not-Fat.	Added Water.
January ...	7·00	17·65	July ...	7·12	16·24
February ...	6·98	17·88	August ...	7·16	15·76
March ...	7·17	15·65	September ...	7·15	15·88
April ...	7·30	14·12	October ...	7·08	16·71
May ...	7·41	12·82	November ...	6·93	18·47
June ...	7·04	17·18	December ...	7·21	15·18

TABLE E.

Month.	Solids-not-Fat.	Added Water.	Month.	Solids-not-Fat.	Added Water.
January ...	7·25	14·70	July ...	7·41	12·82
February ...	7·53	11·41	August ...	7·65	10·00
March ...	7·43	12·59	September ...	7·49	11·88
April ...	7·46	12·24	October ...	7·16	15·76
May ...	7·61	10·47	November ...	7·22	15·06
June ...	7·29	14·24	December ...	7·49	11·88

The highest percentage of added water was found in a sample received during the month of July, and the next two during the months of October and November; the samples containing 8·5 per cent. or over of solids-not-fat were received during the months of January, March, May, June, November, and December. From this one is compelled to conclude that it is possible to produce buttermilk in practically every month of the year without the addition of any water whatsoever.

34, JOHN DALTON STREET,
MANCHESTER.

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NOTE ON THE OIL OF *CERATOTHECA SESAMOIDES*.

By E. RICHARDS BOLTON, F.I.C.

(Read at the Meeting, June 4, 1919.)

Ceratotherca sesamoides is closely allied to *Sesamum indicum* (Gingelly), and the specimen I have examined came from the Gold Coast, where it is known under the name of "Bungu."

These seeds resemble the white *Sesamum indicum* in general appearance, but are rather reddish brown in colour besides being larger than the latter, the weight of 100 seeds being 0·34 and 0·24 grms. respectively. The seeds are rather flatter than those of *Sesamum indicum*, and the edge, which is darker in colour than the rest of the seed, has a serrated appearance.

On extraction with petroleum ether, the seeds yield 35.47 per cent. of a pale yellow oil with a slight nutty flavour. The oil deposits some " stearine " on standing. The following analytical figures were obtained for the oil :

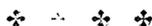
Saponification value	190.20
Unsaponifiable matter	1.53 per cent.
Iodine value	110.60
Refractive index at 40°C., Zeiss	59.60
Free fatty acids (as oleic)	0.63 per cent.
Specific gravity 15/15°C.	0.9163
Baudouin reaction	negative.
Halphen reaction	negative.

The fact that the Baudouin reaction, which is such a delicate colour test for *Sesamum indicum*, is negative is remarkable, since *Ceratotherca sesamoides* is closely allied to *Sesamum indicum*. One would have expected it to be positive, as in the case of the Halphen test for Cotton seed oil, which is also given by Kapok oil, the tree from which the latter is derived being less closely allied to the cotton plant than *Ceratotherca sesamoides* to *Sesamum indicum*.

The other results obtained with this oil are within the limits for sesamé oil, although the specific gravity is slightly lower.

The oil is known to be edible, and would doubtless be of commercial value for use in margarine, etc., if the seed could be collected in sufficiently large quantities. The low free fatty acid content and comparatively slight taste would commend it to the manufacturer of edible oils.

The author's thanks are due to the Director of the Royal Botanic Gardens, Kew, for the specimen examined and for its botanical recognition.



NOTES.

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.

A MODIFIED " ETCHING " TEST FOR FLUORIDES.

The idea for a simplified test for fluorides came from a paper by P. A. Ellis Richards ("The Action of Weak Acids on Soluble Fluorides," *ANALYST*, 1914, **39**, 248), who showed that very weak acids will liberate hydrofluoric acid from sodium and potassium fluorides, in 1 per cent. solutions, employing for the purpose of the test watch-glasses waxed and marked on the concave surfaces.

My first attempts were designed to produce an etched ring round a test-tube from quantities of 10 and 20 mgrms. of sodium fluoride. If 0.010 gm. of sodium fluoride is treated in a test-tube with dilute sulphuric acid (3.5, and 10 per cent. strengths were used), the surface covered with butter-fat or olive oil, and the tube

left on top of a water-oven for three to five days, an etched ring most sharply defined where the junction of fat and acid had been is seen on cleaning. Immersion in hot water for an hour or two prior to removal of contents either intensifies or extends the etching. The time required was an obvious disadvantage.

In the next series of experiments, 10 or 20 mgrms. of sodium fluoride were treated in a test-tube with strong (either commercial or pure) sulphuric acid, and covered either with *Paraffinum liquidum* (B. P.), vaseline, or melted *Paraffinum durum*. After gas production had been going on for a little while, the tubes were placed in hot water. The results were erratic: sometimes a ring was obtained at the junction of paraffin and acid, but more often the glass remained unaffected. It is doubtful whether failures were due to absence of sufficient moisture, or to the viscosity of the concentrated acid forbidding contact of gas and glass.

The following method has always given a result with 0.010 grm. of sodium fluoride. Two or 3 c.c. of 25 per cent. (vol./vol.) sulphuric acid are added and covered with a layer of butter-fat. The test-tube is kept upright in a bath of water (80° to 95° C.) for three hours. The tube is cleaned and dried and a positive test consists of an etching where the acid liquid had contact.

For the test, the tubes are cleaned first with boiling hydrochloric acid, then with boiling alcohol, then left in the water-oven till perfectly dry, any then showing stains or etches being rejected. False "etches" are revealed by successive treatments with ether, boiling alcohol, and boiling hydrochloric acid, and rubbing with a piece of wood.

A control experiment will show whether the acid is free from hydrofluoric acid.

The one volume to three of water strength of sulphuric acid was selected as being somewhat stronger than that of one volume diluted with four volumes of water which is said by C. E. Avery (Crookes, *Select Methods in Chemical Analysis*, p. 624) to decompose felspar and glass "when mixed with the sodium, barium, aluminium, and lead fluorides, or the double fluorides of these metals."

Test-tubes from seven different sources have been used in the tests, including some stout glass made for bacteriological purposes. It seems possible that some glass will etch more readily with small quantities of hydrofluoric acid than others.

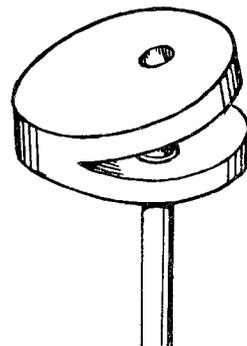
WILLIAM PARTRIDGE.

30, GREAT JAMES STREET,
BEDFORD ROW, W.C. 1.

B.P. QUANTITATIVE LIMIT TEST FOR ARSENIC.

The method of attaching the mercuric chloride paper to the glass tube with a rubber band has been found to give unsatisfactory results, owing to the creasing of the paper preventing a uniform circular stain being produced. The arrangement here described has been found useful and has the merit of being easily prepared; moreover, it is attached to the standard form of apparatus without modification.

A grey india rubber stopper (1 $\frac{3}{8}$ inch) is cut into three "slices" about five-eighths of an inch thick in planes parallel to the ends; each of these "slices" is used to prepare one of the attachments for the arsenic apparatus. The rubber is pierced with a hole just large enough to allow the glass tube of the apparatus to be passed through it, the hole being bored slightly to one side of the centre. The rubber is then slit in a plane parallel to the ends for about two-thirds of its width, and the glass tube passed through the hole in the lower part of it, the widened mouth of the tube is projecting slightly within the slit.



In performing a test a small piece of mercuric chloride paper is placed over the mouth of the tube, the two parts of the rubber are pressed together, and two clips are

applied to hold the paper firmly in position and prevent any escape of gas through the slit. Screw clips have been found suitable for the purpose.

E. GABRIEL JONES.

CITY ANALYST'S LABORATORIES,
LIVERPOOL.



ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Reaction of Aconitine. L. P. J. Palet. (*J. Pharm. Chim.*, 1919, **19**, 295-296.)—The red coloration, described by Dragendorff as characteristic of the alkaloid, produced when aconitine is heated with phosphoric acid solution, is usually only obtained with amorphous products. Pure crystalline aconitine heated with phosphoric acid (sp. gr. 1.7) gives only a faint violet grey coloration. By using a mixture of phosphoric acid (25 grms.) and sodium molybdate (1 gm.), a brilliant violet coloration is obtained with samples of crystalline aconitine which give no coloration with phosphoric acid alone. Of other common alkaloids the only ones which give colorations that could be mistaken for the aconitine reaction are aspidospermine (deep violet) and veratrine (violet-red). The first may be distinguished from aconitine by the action of oxidising agents, and the second by the action of mineral acids.

C. A. M.

Rapp's Method for the Estimation of Alkaloids. K. Dieterich. (*Pharm.-Zeit.*, 1918, **63**, 628-629; *through J. Soc. Chem. Ind.*, 1919, **38**, 336 A.)—Rapp's method has given extremely satisfactory results, but it is important that the quantity of plaster added should be such that the mixture does not harden but remains as a soft paste. It is desirable to make a preliminary blank trial with the plaster to be employed. In the original method it is necessary to make sure by an extra shaking with 10 c.c. of chloroform that all the alkaloid has been extracted from the mass. This uncertainty may be avoided by dissolving the alkaloid first with chloroform before adding the plaster and then using an aliquot portion of the filtered extract for the estimation. For instance, in the valuation of cinchona bark, the substance is treated with the quantity of liquid recommended by Rapp and then shaken in the same flask with 50 c.c. of chloroform, made alkaline, and shaken with 25 grms. of plaster of Paris. The chloroform is then filtered off, and the filtrate 42-45 c.c. shaken with $\frac{N}{10}$ acid. The plaster paste in this method may be of any degree of stiffness, as it does not have to be washed out, all the alkaloid having been dissolved by the chloroform before the addition of the plaster. It is suggested that the principle of Rapp's method might be extended to other extraction operations besides those with alkaloids, since the plaster has a clarifying effect and assists the separation of the extract.

Estimation of Crude Fibre in Cocoa. T. von Fellenberg. (*Mitt. Schweiz. Gesundheitsamt*, 1918, 277; *Ann. Chim. anal.*, 1919, 1, 162.)—One grm. of cocoa or 2 grms. of chocolate are extracted with ether and dried in the water-oven, and then added, together with 30 c.c. of nitric acid, to 120 c.c. of boiling nitric acid. The mixture is boiled for ten minutes, with constant stirring, and filtered through a tarred filter or Gooch crucible containing asbestos. The residue is washed successively with hot water, 1 per cent. sodium hydroxide solution, hot water, hot nitric acid, water and ammonia solution. Finally it is washed several times with hot water, then twice with alcohol and with ether, dried for an hour in the water-oven and weighed. After deducting the weight of the ash in the residue, the result gives the amount of crude cellulose free from lignin. By this method cacao beans of different origin yielded from 3.68 to 5.27 per cent. of crude fibre, with an average of 4.4 per cent., whilst shells yielded 9.5 to 22.04 per cent.; average 18.3 per cent. Cocoa yielding more than 5.5 per cent., calculated on the dry, fat-free material, is to be regarded as adulterated. C. A. M.

Artificial Honey. A. Behre and H. Ehrecke. (*Chem. Zeit.*, 1919, 43, 153-155.)—Analyses of fifty-eight samples of artificial honey are recorded. The water content in nearly all the samples varied from 18 to 20 per cent.; the quantity on uninverted cane sugar was usually under 20 per cent., but in not a few cases it exceeded 25 per cent.; the acidity varied from 0.2 to 4.6 c.c. $\frac{N}{100}$ per 100 grms. The manufacturers aim to produce a solid product, and this condition is governed mainly by the water content of the product and the amount of uninverted cane sugar present. With 20 to 23 per cent. of water and 2 to 6 per cent. of cane sugar, a solid product is usually obtained; if more cane sugar is present, the product remains liquid. The limiting quantity of cane sugar for this amount of water appears to be about 10 per cent. With more than 30 per cent. of cane sugar the product is always liquid. The temperature for the inversion of the cane sugar should not exceed 85° C., whilst the time required depends on the vessel employed (open or closed), the acidity, stirring, etc. The suggestion is made that the addition of some substance such as starch or phenolphthalein to artificial honey should be made compulsory in order to render easy the detection of artificial honey in natural honey. W. P. S.

Iodine Value (Wijs) of Palm Kernel Oil. R. H. Ellis and E. M. Hall. (*J. Soc. Chem. Ind.*, 1919, 38, 128 T.)—The normal range of iodine values for palm kernel oil is 16 to 23. The average value for 574 samples of refined oil was 18.1, and for 1236 samples of crude oil 18.6; these oils were expressed from the kernels crushed in the mill under ordinary works conditions. W. P. S.

Estimation of Lactose and Proteins in Milks Preserved with Potassium Dichromate. P. Defrance. (*Ann. Falsific.*, 1919, 11, 78-79.)—The polarimetric estimation of lactose in milk preserved with potassium dichromate is unreliable, since the quantity of the sugar found decreases gradually until after about seventy days only 50 per cent. of the amount originally present is obtained. The amount of lactose does not, however, show any diminution during this period, when it is

estimated by determining its copper-reducing power. The casein in milk treated with dichromate also undergoes considerable alteration; whilst the quantity of total protein remains the same, the casein (protein precipitated by acetic acid) decreases from 2.58 to 2.10 per cent. in forty-four days.

W. P. S.

Analysis of Prune Kernels. L. Fordyce and D. M. Torrance. (*Chem. News*, 1919, **118**, 242-243.)—Prune kernels yielded 42 per cent. of oil, 2.47 per cent. of nitrogen, and 37.42 per cent. of sugars. The oil, when cooled at -5°C ., partially solidified, the solid portion amounting to about one-third of the whole. The solid portion had sp. gr. 0.9055 and saponification value 239.8; the liquid portion had sp. gr. 0.9119 and saponification value 207.4. The sugars present were lævulose and dextrose and, possibly, cane sugar.

W. P. S.

Rapid Estimation of Tartaric Acid in Wines. L. Mathieu. (*Ann. Falsific.*, 1919, **11**, 80-81.)—The author recommends a method described originally by Pasteur in 1873. Twenty c.c. of the wine are treated with a quantity of *l*-tartaric acid (in the form of a 1 per cent. ammonium *l*-tartrate solution) equivalent to the amount of potassium hydrogen tartrate contained in the 20 c.c. of the sample. For instance, 5.87 c.c. of the solution are required when the wine contains 3 grms. of potassium hydrogen tartrate per litre. A quantity of calcium hydroxide solution, sufficient to neutralise the 20 c.c. of wine, is then added, and, after a few minutes, the precipitated calcium racemate is filtered off; two equal portions of the filtrate, say 15 c.c. each, are then treated separately, the one (*A*) with a few drops of 1 per cent. ammonium *d*-tartrate solution and the other (*B*) with a few drops of ammonium *l*-tartrate solution. If, after the lapse of one hour, both mixtures remain clear, the wine contained exactly the amount of potassium hydrogen tartrate which would correspond with the quantity of *l*-tartaric acid added originally. Should a precipitate form in *A*, the wine contains less than this quantity of potassium hydrogen tartrate; if a precipitate forms in *B*, more than this quantity is present. Further quantities of 20 c.c. of the wine are then treated with more or less of the *l*-tartaric acid solution, as the case may be, until the quantity of potassium hydrogen tartrate is ascertained within narrow limits. A solution of 16 grms. of calcium carbonate in 120 grms. of acetic acid and diluted to 1 litre may be used in place of the calcium hydroxide solution. The total tartaric acid in the wine is expressed as potassium hydrogen tartrate.

W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Sampling Field Plots for Bacteriological Examination. H. A. Noyes and E. Voight (*Abst. of Bact.*, 1918, **2**, 3-4; *Bull. Agric. Intell.*, 1919, **10**, 38-39.)—In sampling for moisture and chemical work the best method is to select a number of spots representative of the soil, the crop, and the method of treatment, and analyse each sample separately; then any variations subsequently developed at these spots are studied in connection with the problem under investigation. In bacteriological work it is not possible to deal with the large number of samples necessary to eliminate experimental errors. The most satisfactory method is to select for bacteriological study

those spots which show uniformity in chemical tests. Samples are taken at regular intervals, care being taken to avoid the cultural disturbance caused by the taking of previous samples; the variations are then recorded in terms of the individual samples rather than as plot averages. As regards the quantity of field soil necessary to be taken for bacteriological analysis, it is remarked that a principal source of error is due to the variation in the size of the particles and the bacterial distribution is a function of the area of the soil particles in the given weight of sample. All the indications go to show that larger samples of soil are required to give reliable results for bacteria than are required for moisture estimations, and since moisture estimations require from 10 to 30 grms. for concordant results, according to the fineness or coarseness of the soil, at least 50 grms. should be taken for the biological test. A larger quantity than 50 grms. has not been found to improve the agreement between triplicate tests, but less than 40 grms. has been found in some cases to cause large variations and less than 25 grms. is definitely unsatisfactory. The authors have adopted 50 grms. of field soil in the natural moist condition as the standard quantity for examination, and mix this with 20 c.c. of sterile distilled water to make the first bacterial dilution.

J. F. B.

Disinfection with Formaldehyde. Practical Efficiency of some Substitutes for the Permanganate-Formalin Method. M. A. Pozen and L. V. Dieter. (*J. Ind. and Eng. Chem.*, 1919, 5, 448-451.)—The purpose of the investigation was to determine on a practical scale the relative efficiency of various reagents proposed to replace expensive permanganate for generating formaldehyde and water vapour from formalin for the disinfection of rooms after contagious and infectious diseases. The following quantities of reagents have been recommended for each 1,000 cubic feet of space.

Dichromate Method.—Sodium dichromate, 10 ounces; formalin, 1 pint; sulphuric acid, $1\frac{1}{2}$ fluid ounces; glycerol, $1\frac{1}{2}$ fluid ounces.

Barium Peroxide Method.—Barium peroxide (78 per cent. BaO_2), $1\frac{1}{2}$ pounds; formalin, 1 pint.

Chlorinated Lime Method (1).—Chlorinated lime, $1\frac{1}{3}$ pounds; formalin, $1\frac{7}{10}$ pints.

Chlorinated Lime Method (2).—Chlorinated lime, $\frac{5}{8}$ pound; formalin, 1 pint.

Sodium Chlorate Method.—Sodium chlorate, 6 ounces; formalin, 1 pint.

Lime Method.—Crushed lime, $1\frac{1}{2}$ pounds; formalin, $1\frac{1}{2}$ pints; sulphuric acid, 2 fluid ounces; magnesium sulphate, $1\frac{3}{4}$ ounces.

Permanganate Method (per 1,000 cubic feet of room space).—Potassium permanganate, $\frac{1}{2}$ pound; formalin, 1 pint.

These were all tried on the laboratory scale before testing on two rooms, each of which was specially prepared, and contained articles of clothing, books, furniture, etc. Bacteriological examinations were subsequently made to determine whether cultures previously placed in the rooms on the furniture, inside books, and so forth, had survived. It was found that the barium peroxide, sodium chlorate, and chlorinated lime methods are all as efficient as the permanganate method. The barium peroxide and the chlorinated lime methods involve simple manipulation. As regards economy, the permanganate method is by far the most expensive, while the lime

methods are cheapest, barium peroxide being about one-third the cost of permanganate. The authors, as a result of their study, are inclined to recommend a chlorinated lime-formalin method (either formula) as the best practical method of those studied for the routine disinfection of rooms.

H. F. E. H.

Estimation of Urea. Philibert. (*J. Pharm. Chim.*, 1919, **19**, 335-346.)—The accuracy of Fosse's gravimetric method of estimating urea (*Ann. de l'Inst. Pasteur*, 1916, **30**, 425) is confirmed. Ten c.c. of the urine, previously filtered and diluted (1:10), are treated with 35 c.c. of glacial acetic acid, and 5 c.c. of a 10 per cent. solution of xanthydrol in absolute methyl alcohol, which is added 1 c.c. at a time, with 10 minutes' interval after each addition. After standing for some hours, the precipitate of dixanthylurea is collected on a tared filter, washed with a little alcohol, dried at 100° to 105° C., and weighed. The weight divided by 7 gives the amount of urea. In comparative estimations, using this method as the criterion, it was found that Folin's method (*Amer. J. Physiol.*, 1905, **12**, 213) was the most trustworthy of the hydrolytic methods, and that the hypobromite method, after defecation with lead, was the best of the gasometric methods. The errors to which Folin's method is liable are due to irregularity of the hydrolysis of the urea, and to unequal hydrolysis of nitrogenous substances other than urea in the urine, whilst quantitative distillation of the ammonia from the magnesia mass is not always easy. The sources of error in the hypobromite method are those of measurement, and especially the degree of agitation during the reaction. Without the use of mercury it is difficult to effect sufficient agitation in the case of dilute solutions of urea, and instruments in which mercury is not used are unsatisfactory.

C. A. M.

Estimation of Urea and Non-protein Nitrogen in Blood and Animal Tissue by means of Nessler's Reagent. A. Grigaut and F. Guérin. (*J. Pharm. Chim.*, 1919, **19**, 233-243; 281-294.)—By a combination of the methods of enzymic hydrolysis by means of urease and estimation of the ammonia by means of Nessler's reagent, urea can be accurately estimated in a small amount of blood. The urease suspension is prepared by triturating 1 gm. of finely sifted soya bean flour with an aqueous solution of 0.4 gm. of sodium hydrogen phosphate, and diluting the liquid to 100 grms. with ammonia-free water. For the Nessler reagent the amount of alkali is reduced to 3 per cent., and alkali subsequently added to the ammoniacal liquid. In this way the formation of turbidity in the reagent is prevented. From 1 to 3 c.c. of serum, plasma, or blood are mixed with twice the volume of the soya meal preparation, and kept at 56° C. for 15 minutes with occasional agitation. The hydrolysed mixture is then shaken with an equal volume of 20 per cent. trichloroacetic acid (to precipitate albumins and the added urease), and filtered. From 1 to 6 c.c. of the filtrate, according to its richness in ammonia, is made up to about 40 c.c. with water, and 3 c.c. of 10 per cent. sodium hydroxide solution (free from sulphates and carbonates) is added. For the comparison a solution containing 0.25 mgrm. of nitrogen with the same proportion of trichloroacetic acid and sodium hydroxide is prepared. To each of the two solutions, which must be thoroughly mixed, is added 5 c.c. of the modified Nessler's reagent (3 per cent. of NaOH, 5 to

6 per cent. of $\text{HgI}_2, 2\text{KI}$), and the colorations are immediately matched in a Duboscq colorimeter. For the estimation of urea in animal tissue this method is unsuitable owing to the presence of creatinine, and it is better to make the estimation by Fosse's xanthidrol method. For the estimation of non-protein nitrogen in blood from 3 to 5 c.c. of the plasma, serum, or blood are mixed with their own volume of 20 per cent. trichloroacetic acid, and filtered after a few minutes. Two c.c. of the filtrate are mixed with 1 c.c. of a mixture of 1 volume of pure sulphuric acid (95.6 per cent.) and 3 volumes of pure phosphoric acid (85.4 per cent.) to which has been added a fifteenth part of the total mixture of 10 per cent. copper sulphate solution. This reagent is filtered after 24 hours through glass-wool. The tube containing the trichloroacetic acid filtrate and the reagent is heated until white fumes appear, and its mouth is then covered and the heat regulated so that the fumes fill the tube but do not escape, until all carbon has disappeared. The liquid is then cooled, made up to 70 to 75 c.c., rendered slightly alkaline, and tested with Nessler's reagent as described above, the standard solution for the comparison having been subjected to the same treatment. For the estimation of non-protein nitrogen in animal tissue the material is extracted with water, albumins precipitated with trichloroacetic acid, and the filtrate treated with the phospho-sulphuric acid mixture as in the case of blood. C. A. M.

ORGANIC ANALYSIS.

Examination of Acetone Oils. W. J. Jones. (*J. Soc. Chem. Ind.*, 1919, 38, 108-110 T.)—Acetone oils contain, in addition to acetone and hydrocarbons, a number of higher ketones of the acetone series, cyclopentanone and acetaldehyde, all of which, with the exception of the hydrocarbons, are soluble in sodium bisulphite solutions. The method of examination differs according to the nature of the material, but in no case is a very high degree of accuracy obtained.

1. *Examination of First Runnings from the Rectification of Crude Acetone.*—About 150 grms. of the oil are dried by anhydrous sodium sulphate. The specific gravity of the oil is determined, as received and after drying. Water is estimated from the volume of the aqueous layer, which separates on mixing 1 volume of the original oil with 2 volumes of benzene or toluene, and is calculated in terms of weight from the specific gravity of the original oil. Reducing substances (acetaldehyde) are determined in the following manner: A known volume of the oil (about 1 c.c.) is measured into a stout bottle, 20 c.c. of concentrated ammonia solution and 100 c.c. of $\frac{\text{N}}{10}$ silver nitrate are added, and the bottle is immersed in a bath of boiling water for eight hours. After cooling, the liquid is diluted to 500 c.c. and the reduced silver filtered off; if the filtrate is coloured, it is treated with animal charcoal and again filtered. The clear filtrate is acidified with nitric acid, and the excess of silver titrated by Volhard's method. The acetone is estimated from the decrease in volume of the dried oil on shaking with 5 volumes of water and correcting for the acetaldehyde.

2. *Examination of Acetone Oils of Higher Boiling-point.*—Specific gravity and water are determined as above. One hundred grms. of the dried oil are placed in a tared flask of 150 c.c. capacity and distilled through an efficient fractionating column.

The following fractions are collected: up to 68° C.; 68° C. to 90° C. and 90° C. to 140° C., if necessary. The distillation residue is also weighed. The methyl ketones are then determined in each fraction by means of sodium bisulphite solution, sp. gr. 1.2 to 1.3. If V_{68} , V_{90} , and V_{140} c.c. are the respective volumes of the separate fractions, a volume of sodium bisulphite equal to three times that of the fraction is added to each, and the mixture is carefully shaken at first with efficient cooling, and then vigorously until no further absorption takes place; then U_{68} , U_{90} , and U_{140} represent the respective volumes of the residual oils. Then the percentage by weight of acetone is calculated from the data $V_{68}-U_{68}$, the percentage of methyl-ethyl ketone from $V_{90}-U_{90}$, and that of higher ketones from $V_{140}-U_{140}$, with due allowance for the respective densities of the ketones and the original oil. The distillation residue does not contain appreciable quantities of reactive substances. The author has made up artificial mixtures of known composition by mixing purified ketones, obtained from acetone oils and subsequently fractionated, with various proportions of non-ketone residues, and has tested the accuracy of the method by analysing these mixtures. The results show a sufficient degree of accuracy to establish the utility of the method. The process for the estimation of water in acetone or methyl-ethyl ketone appears to be quite satisfactory. J. F. B.

Albuminoid Ammonia Test. E. A. Cooper and J. A. Heward. (*Biochem. J.*, 1919, 13, 25-27).—Potassium permanganate may contain a stable nitrogenous impurity which cannot as a rule be removed by prolonged boiling with alkali. The impurity is not decomposed in concentrated alkaline solution, but gradually decomposes when the solution is considerably diluted. Consequently, permanganate-alkali mixture can apparently be freed from ammonia by boiling with water, but when the resulting concentrated solution is again diluted and distilled, ammonia may once more be liberated in large quantities. When the mixture, apparently freed from ammonia, is boiled with the water, the albuminoid ammonia figure of which is being determined, the yield of ammonia is thus greatly augmented by that liberated from the permanganate. The error involved may be so great (0.02 parts per 100,000) as to vitiate the value of the albuminoid ammonia test altogether. In the case of a purer brand of permanganate the error is reduced to about 0.002 parts albuminoid ammonia per 100,000. It is essential in routine work to test fresh supplies of chemicals to ensure that the impurity is not present in excessive amount, and in very accurate work a control experiment should be made during each determination of albuminoid ammonia. H. F. E. H.

Recovery of Alcohol from Potash Estimations. A. E. Smoll. (*J. Ind. and Eng. Chem.*, 1919, 5, 466-467).—At the present price of alcohol it is economical to recover it when large numbers of potash estimations are made by the platinum method. If the alcohol is distilled off it is found that the slight amount of acetaldehyde arising has a tendency to lower the potash results in subsequent estimations. The author recommends that the distillation be carried out on an electric hot plate until the boiling-point of the distillate is 100° C., by which time the platinum has all been reduced and can be washed and treated further in its recovery as in the method where zinc and

hydrochloric acid are employed. To effect the removal of the aldehyde from the alcohol fractional distillation is adopted, the flask being connected directly with an Allihn condenser, which serves the purpose of a reflux condenser. Warm water should be run through the Allihn condenser and should be so regulated that the temperature at the outlet is 58° C., this being hot enough to allow the aldehyde to escape, while at the same time condensing the alcohol, provided the boiling is not too vigorous. The distillation is continued until no trace of aldehyde comes over, this being easily tested for by mixing a few crystals of phenol with 5 c.c. of concentrated sulphuric acid. If there is a trace of aldehyde this will give a reddish-brown solution with the phenol mixture. The remaining alcohol, when free from aldehyde, can then be collected and, if necessary, redistilled from caustic soda.

H. F. E. H.

Detection of Renatured Alcohol in Spirits. L. Wolfrum and J. Pinnow.

(*Zeitsch. Untersuch. Nahr. Genussm.*, 1918, **36**, 270-273; through *J. Soc. Chem. Ind.*, 1919, **38**, 383 A.)—The removal of pyridine from denatured alcohol is not a difficult matter; the resulting spirit would still contain methyl alcohol, acetone, allyl alcohol, empyreumatic substances, etc., but it is possible that it might be used to adulterate brandy, etc. Fendler and Mannich's reaction (conversion of the methyl alcohol into formaldehyde and detection of the latter by means of morphine dissolved in concentrated sulphuric acid) may be used for detecting the presence of such renatured alcohol, since it will indicate with certainty 6 per cent. of methyl alcohol in ethyl alcohol. If ethyl alcohol containing a small percentage of methyl alcohol is distilled until its volume is reduced to one-half, the distillate will contain 70 per cent. of the methyl alcohol.

Detection of Methyl Alcohol in Ethyl Alcohol. E. Salkowski. (*Zeitsch.*

Untersuch. Nahr. Genussm., 1918, **36**, 262-270; through *J. Soc. Chem. Ind.*, 1919, **38**, 382 A.)—A test for methyl alcohol depends on its oxidation, and detection of the resulting formaldehyde. The ethyl alcohol to be tested is diluted with 9 volumes of water, and 0.5 c.c. of this mixture is treated with 3 c.c. of dilute sulphuric acid and 3 c.c. of 1 per cent. potassium permanganate solution. After eight minutes, the solution is decolourised with saturated oxalic acid solution, distilled, and the distillate heated to boiling with the addition of 0.08 gm. of peptone, 3 drops of 3 per cent. ferric chloride solution, and its own volume of hydrochloric acid (sp. gr. 1.19). If the original alcohol contained as little as 1 per cent. of methyl alcohol, a bright violet coloration develops. This, and other tests which are based on the formation and detection of formaldehyde are reliable when dealing with methyl and ethyl alcohols alone, since the latter does not yield formaldehyde on oxidation. Higher alcohols, such as propyl, isobutyl, and isoamyl alcohols, yield distinct traces of formaldehyde when treated as above, and the presence of these alcohols in commercial ethyl alcohol might lead to the erroneous conclusion that methyl alcohol was present. In the deliberate adulteration of alcohol with methyl alcohol, quantities of less than 10 per cent. of the latter are not likely to be used; the strong coloration given by this proportion of methyl alcohol would be almost conclusive evidence of adulteration,

since the colorations yielded by the small quantities of higher alcohols which might be present in ethyl alcohol would be much less intense.

Estimation of Benzene in Crude Benzols. W. J. Jones. (*J. Soc. Chem. Ind.*, 1919, **38**, 128-130 T.)—The sample is diluted with a quantity of pure benzene sufficient to bring the freezing-point of the mixture up to region 0° to 1° C. From the weights of crude benzol and benzene used and from the freezing-points of the mixture and the benzene, the benzene content, x , of the crude benzol can be calculated from the formula: $x = 90.68 + 1.73t$, where t is the freezing-point of the mixture.
W. P. S.

Estimation of Phenol in Tar Oils. G. C. Petrie. (*J. Soc. Chem. Ind.*, 1919, **38**, 132-133 T.)—A modification of Fox and Barker's method (*ANALYST*, 1917, **42**, 329; 1918, **43**, 389) is described. It was found that calcium chloride, plaster of Paris, and anhydrous sodium sulphate did not extract all the moisture from phenolic mixtures. The mixture is dissolved in twice its volume of benzene and extracted with 10 per cent. sodium hydroxide solution; the alkaline solution is steam-distilled to remove neutral oil and naphthalene, then cooled, acidified with dilute sulphuric acid, and, after four hours, the aqueous portion is separated from the phenol acids and extracted three times with benzene, using 90 c.c. in all. The benzene solution is added to the phenol acids, any water which separates is drawn off, and the mixture is fractionated through a Young's 12-pear head. Water with some benzene distils off at about 75° C., the remaining benzene passes over practically free from water, and phenol commences to distil at about 180° C.; the first few drops of the phenol distillate are discarded, and the distillate up to 195° C. is then collected in a weighed receiver from which moisture is excluded. The percentage of phenol in this distillate is estimated by the freezing-point method described (*loc. cit.*).
W. P. S.

Estimation of Traces of Phosgene (Carbonyl Chloride) in Air. A. Kling and R. Schmutz. (*Comptes rend.*, 1919, **168**, 891-893.)—When air containing phosgene in as small proportion as 1:100,000 is passed through a cold saturated aqueous aniline solution, the phosgene is absorbed completely, and a distinct precipitate of diphenylcarbamide is obtained. To estimate the quantity of phosgene present, from 1 to 5 litres of the air are passed slowly (bubble by bubble) through 10 c.c. of aniline solution. If the quantity of phosgene is suspected to be large (up to 2 per cent.) a second absorption vessel containing aniline solution should be used in series with the first. The precipitate of diphenylcarbamide is collected on a small filter, washed a few times with the minimum quantity of water, dried at 60° C. for two hours to remove excess of aniline, then dissolved in boiling alcohol, the solution evaporated at a low temperature, the residue dried at 60° C. for two hours, and weighed. When the amount of precipitate is very small, the filter and precipitate should be digested with sulphuric acid and mercury, as in Kjeldahl's process, the ammonia formed distilled, and its quantity estimated by means of Nessler's reagent (*cf. ANALYST*, 1919, 207).
W. P. S.

INORGANIC ANALYSIS.

Influence of Various Ammonium Salts on the Precipitation of Magnesium Hydroxide. E. Brunner. (*Helv. Chim. Acta*, 1919, 2, 277-279.)—It is shown that ammonium sulphate is much more effective than ammonium chloride in holding up magnesium hydroxide, a fact which conflicts with the theory offered in many textbooks to explain the hindrance which ammonium salts exercise on the precipitation of magnesium hydroxide. Attempts to apply the new knowledge to the separation of calcium and magnesium were unsuccessful. Apart from the fact that, in presence of sulphates, solutions of calcium salts must be highly diluted, which is inconvenient, the author has failed to obtain exact or even concordant results.
G. C. J.

Estimation of Free Carbonic Acid in Water. R. Czerny. (*Zeitsch. anal. Chem.*, 1919, 58, 1-12.)—Free carbonic acid in water is estimated by titration with sodium carbonate solution in the presence of phenolphthalein. The neutral point corresponds to the bicarbonate, but in order to arrive at the same point it is necessary to vary the amount of indicator in proportion to the amount of bicarbonate present. This is most conveniently attained by adding a substantial quantity of phenolphthalein to the standard sodium carbonate solution employed. A series of experiments was made with water of increasing degree of carbonate hardness to compare the results of this titration method with those obtained by Winkler's standard method. The results proved that the number of c.c. of sodium carbonate-phenolphthalein solution required was proportional to the amount of free carbonic acid in the water. The accuracy of the results is not affected by the alkalinity (bicarbonate) of the water. Nevertheless, using $\frac{N}{20}$ sodium carbonate solution, it was always found that about 0.5 c.c. was required before any indication was shown, and this amount is deducted as a constant correction for the zero-point of the titration. The comparative estimations against Winkler's method showed an average error of +1 mgrm. of CO_2 per litre, and a proportional correction should be applied to adjust this. The method, therefore, is described as follows: The standard $\frac{N}{20}$ soda solution is made by dissolving 2.6525 grms. of pure sodium carbonate and 2.5 grms. of phenolphthalein in boiled distilled water and making up to 1 litre. One hundred c.c. of the water to be tested are titrated with this solution to a permanent pink colour. The zero-point correction of 0.52 c.c. is deducted from the number of c.c. used, and the remainder is multiplied by the factor 1.22 (instead of the theoretical 1.1) in order to calculate the mgrms. of free CO_2 in 100 c.c. of the water.
J. F. B.

Metallic Ferrocyanides, their Behaviour towards Chlorine and Bromine in Aqueous Solution and their Application in Analytical Chemistry. F. F. Werner. (*Zeitsch. anal. Chem.*, 1919, 58, 23-24.)—Zinc ferrocyanide is frequently employed in analytical operations, and behaves in a characteristic manner when treated with bromine water. Manganese ferrocyanide is white and sparingly soluble; on oxidation with chlorine water it is coloured grey; bromine water converts it into the brown ferricyanide. Nickel ferrocyanide is bluish-green, and the precipitate is

applicable both for gravimetric and volumetric analysis. It is not readily changed by chlorine water, but bromine converts it into the brown ferricyanide. Cobalt ferrocyanide is dirty green in colour but extremely unstable, and undergoes a change in contact with the air. Chlorine water converts it into ferricyanide, and bromine water decomposes it entirely with separation of black cobalt hydroxide. Mercurous ferrocyanide is greyish-white, sparingly soluble; it changes to green with chlorine water and greenish-yellow with bromine water, but is not converted into the ferricyanide. Mercuric ferrocyanide is white, and is turned green by chlorine water, brown by bromine water. Bismuth ferrocyanide is deep yellowish-green and almost completely insoluble; it is the most stable of this group of compounds, and is not appreciably oxidised by chlorine or bromine water. The reactions above described are capable of analytical application in the case of cobalt, nickel, and bismuth.

J. F. B.

Continuous Process for the Estimation of Nitrogen by Dumas' Method.

L. Dexheimer. (*Zeitsch. anal. Chem.*, 1919, **58**, 13-19.)—One of the drawbacks of the highly accurate Dumas' method is the length of time occupied in cooling the tube between one estimation and the next. The author has devised a method of continuous operation which avoids this necessity, and enables 15-20 estimations of nitrogen to be carried out in a day. After the end of the first combustion the current of carbon dioxide is sent through the tube in the reverse direction, and the flame under the hinder portion of the tube is extinguished as far as the granulated cupric oxide. The latter and the copper spiral are heated continuously during a series of estimations. The reversal of the carbon-dioxide current prevents the access of air during the operation of withdrawing the combustion boat and the plug of copper oxide at the hinder end and the substitution of a fresh boat and fresh plug of copper oxide, which are kept ready. In order to prevent the immediate volatilisation of the new substance the combustion tube should project 15-20 cm. beyond the furnace at this end, and this portion of the tube is always cold. When the boat has been inserted in this portion and the stopper of the tube replaced, the current of carbon-dioxide is again passed in the forward direction and a fresh nitrometer is fitted to the apparatus. The absence of air is next confirmed by means of this nitrometer, and as soon as this is indicated, the boat is pushed forward into the combustion zone. After two or three estimations it becomes necessary to regenerate the copper oxide by passing a current of oxygen through the tube in the reverse direction, and this is so arranged that it is introduced through a capillary tube which passes through the copper spiral so that the latter is not oxidised. The passage of oxygen is performed at the same time as the current of carbon-dioxide is reversed, and the excess of oxygen is subsequently swept out by the carbon dioxide. The manipulation of the boat is effected by a wire with a loop at the end which is passed through the stopper of the combustion tube and is lubricated with glycerol.

J. F. B.

Estimation of Phosphorus in Phosphor Tin. **W. Lord.** (*Chem. News*, 1919, **118**, 254.)—The finely divided metal (1 gram.) is treated with nitric acid in a crucible

and heated on a water bath until oxidation is complete. The mass is taken to complete dryness and mixed with six times its weight of pure potassium cyanide. The covered crucible is heated to dull redness for 15 minutes. When cold the melt is extracted with steam by placing the crucible upright in a beaker and directing a jet of steam at it. Five minutes serve for the extraction when conducted in this manner. The button of tin is filtered off and the filtrate acidulated with hydrochloric acid to decompose potassium cyanide and cyanate. After boiling to expel hydrogen cyanide, a rapid stream of hydrogen sulphide is led through the solution to precipitate any tin which may have escaped separation as metal. After filtering if necessary, bromine water is added and the solution concentrated to 50 c.c., cooled, and made slightly ammoniacal. If any precipitate forms, it is filtered off, dissolved in hydrochloric acid, reprecipitated, and the filtrate added to the main solution, to which 10 c.c. of magnesia mixture are now added. The mixture is stirred until crystals begin to form, when 10 c.c. of ammonia are added and the mixture left at rest overnight. The precipitate is collected on asbestos, washed with 2 per cent. ammonia containing ammonium nitrate, dried in an air bath, and finally ignited at the back of a muffle.

G. C. J.

Volumetric Estimation of Sulphates. A. C. D. Rivett. (*Chem. News*, 1919, 118, 253-254.)—Although of limited applicability, the following method has proved useful. It depends on the fact that moist precipitated barium oxalate reacts quantitatively with the soluble sulphates of certain metals. The solution to be tested must not be acid, nor contain the sulphates of metals forming insoluble oxalates, nor salts containing radicles capable of forming insoluble barium salts. It is convenient to take so much of the solution as contains from 1 to 2 grms. of sodium sulphate or its equivalent and to dilute this to about 150 c.c. About three times as much barium oxalate as is equivalent to the sulphate present is next added and the mixture boiled for 5 minutes. It is then cooled, made up to 200 or 250 c.c., filtered, and an aliquot of the filtrate titrated with permanganate. A correction is made for the volume of the precipitate. If more than 2 grms. of sulphate are present in the original 150 c.c., the solution must be boiled longer than 5 minutes to ensure satisfactory accuracy. If less than 0.75 gm. is present, the error due to the solubility of barium oxalate exceeds 0.5 per cent. In presence of large proportions of nitrate the results may be 5 per cent. too high, but on a works liquor of tolerably constant composition it is easy to establish a correction factor for this and obtain results accurate to within 0.5 per cent.

G. C. J.

Estimation of Sulphates as Strontium Sulphate. J. M. Kolthoff and E. H. Vogelenzang. (*Zeitsch. anal. Chem.*, 1919, 58, 20-23.)—The authors have investigated the method for the gravimetric estimation of sulphates by precipitation with strontium chloride. It was established that strontium sulphate is quite insoluble in 30 per cent. alcohol, and the precipitations were carried out in the presence of an equal volume of alcohol; the solubility was, however, greatly increased by the presence of hydrochloric acid and salts, particularly ammonium salts. In the absence of salts the results came out rather high, apparently owing to the occlusion of the

reagent by the precipitate. In the presence of hydrochloric acid the results were very low (error of 5 per cent.), but were considerably better when the free mineral acid was neutralised by sodium acetate. Ammonium chloride and sodium chloride gave very low results. In the case of ammonium salts, it is inferred that a double strontium ammonium sulphate is present in the precipitate, and ammonium sulphate is volatilised from this on ignition. Sodium nitrate is less injurious than sodium chloride. Ferric salts also interfere with the accuracy of the results by this method as well as by the barium sulphate method. The authors conclude that the strontium method is incapable of giving satisfactory results. J. F. B.

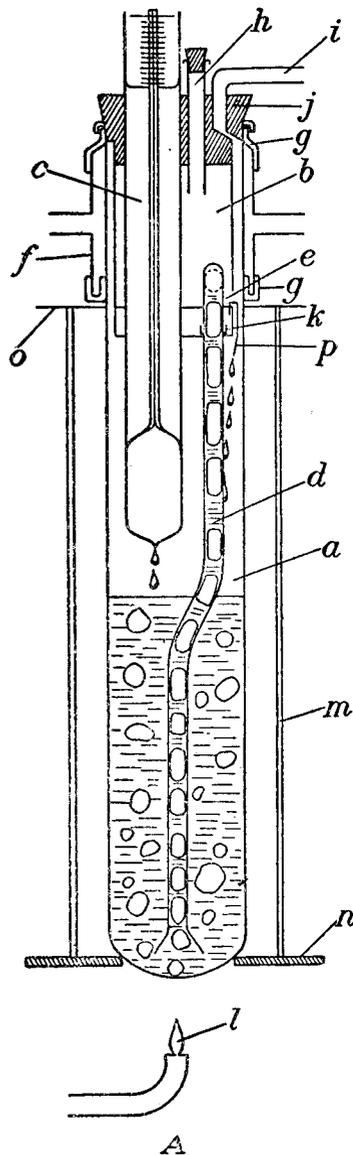
Detection of the More Important Oxidised Sulphur Compounds. A. Sander. (*Chem. Zeit.*, 1919, 43, 173.)—An extension of the use of mercuric chloride as a reagent for the detection of thiosulphates and other oxidised sulphur compounds is described. When this reagent is added to a solution of sodium sulphate the solution remains neutral and no precipitate forms. In the cold sulphite solutions give no precipitate, and remain alkaline to methyl orange as before the addition of the reagent, but on heating mercurous chloride separates and sulphur dioxide is liberated. Bisulphite solutions behave similarly, except that they become strongly acid even before heating, as hydrogen chloride is one of the products of the first reaction in the cold. If sulphides are present, a black precipitate of mercuric sulphide forms at first, but on the addition of excess of mercuric chloride this is transformed into the yellowish-white double salt $2\text{HgS} \cdot \text{HgCl}_2$. Excess of mercuric chloride is always added as the further examination of the supernatant liquor is then simplified. Thiosulphates behave like sulphides except that in the case of thiosulphates the solution becomes strongly acid. Polythionates behave like thiosulphates, from which they can be distinguished by the fact that they do not reduce iodine. G. C. J.

APPARATUS, ETC.

Use of Mercury Vapour Lamps for Laboratory Tests. M. Entat. (*Ann. Chim. anal.*, 1919, 1, 142-153.)—An apparatus is described for testing the action of ultra-violet rays on textiles, plastic substances, dyes, etc. The fabric, etc., is made to travel on an endless band at a regulated speed beneath a mercury vapour lamp fixed at such a radius that all parts of the material receive an equal quantity of rays. By experiments under constant conditions it was found that a quantitative relationship could be established between the effects of direct sunshine and of ultra-violet rays. For example, the breaking strain of silk fabrics was reduced to the same extent by two to four hours' exposure to the rays of the mercury vapour lamp as by thirty days' insolation. The breaking strain of undyed silk was reduced by 34.9 per cent. by the exposure to ultra-violet rays, but the action of the rays was reduced by 15 to 23 per cent. by dyeing the silk with various dyestuffs. After two hours' exposure the *coefficients of protection* afforded by different dyestuffs were as follows: Uranine, 15; malachite green, 17; methyl violet, 18; orange III., 19; methylene blue, 22; and quinoleine red, 23. C. A. M.

Apparatus for Determination of Boiling-Points of Solutions. F. G. Cottrell. (*J. Amer. Chem. Soc.*, 1919, **41**, 721-729.)

The novel feature of the apparatus consists in placing the thermometer bulb in the gas phase as in the case of a pure liquid, and making the boiling of the liquid itself pump some of the latter mechanically in a thin film over it, thus duplicating as far as possible the same relations of gas, liquid, and thermometer which ordinarily obtain in boiling-point determinations of pure substances. The solution is boiled in *a*, a large test-tube; *b* is a flat-bottomed specimen tube in whose bottom two holes have been blown or ground. Through these holes pass loosely the Beckmann thermometer *c* and the pump tube *d*, the thermometer as well as the tube *b* being entirely supported by the stopper *j*, while the tube *d* rests upon its shoulder *k* formed by softening the tube at this point and pushing it slightly together from opposite ends. A moderate leak under the shoulder is of no consequence. As an alternative to this shoulder, a few turns of stout platinum wire helix, fitting the tube snugly, may be slipped over it at this point; this has the advantage of allowing adjustment of height and of permitting the removal of *d* from *b* at this end. Another hole *e* is also provided in the side of *b* farthest from *c* to equalise gas pressure between *a* and *b*, and act as an overflow. The water jacket *f* secured by the rubber tubing *g* to the upper part of *a* forms, with the latter, the reflux condenser. The tube *h* is for the introduction of the solute. The tube *i* connects through a number of radiating channels bored or burned through the stopper *j* with the annular condensing space between *a* and *b*, and serves to equalise the pressure between the vapour space of the apparatus and the outside. The liquid is boiled by the gas-flame *l*. The portion of the test-tube below the condenser is protected from draught by the glass tube *m* resting on the asbestos plate *n*, and closed above by the perforated mica plate *o*. To prevent the squirting of liquid against the stopper *j*, the upper end of *d* is sealed and a hole blown in its side. A short piece of glass rod or platinum wire *p* is hooked into the overflow hole *e* and allowed to extend slightly below the bottom of *b*. The pump tube may be 2 mm. in diameter for ether and other liquids of small surface tension, but for water is better made 4 mm. In practice the length of *d* above the liquid should be some-

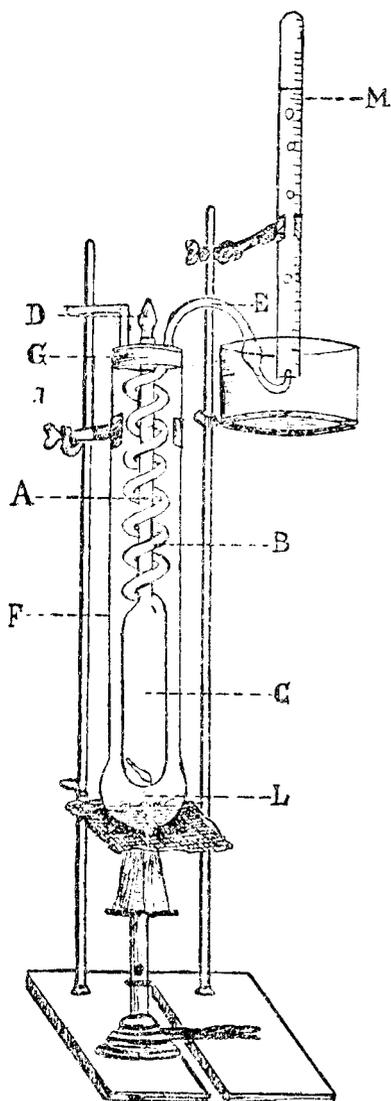


A

of the test-tube below the condenser is protected from draught by the glass tube *m* resting on the asbestos plate *n*, and closed above by the perforated mica plate *o*. To prevent the squirting of liquid against the stopper *j*, the upper end of *d* is sealed and a hole blown in its side. A short piece of glass rod or platinum wire *p* is hooked into the overflow hole *e* and allowed to extend slightly below the bottom of *b*. The pump tube may be 2 mm. in diameter for ether and other liquids of small surface tension, but for water is better made 4 mm. In practice the length of *d* above the liquid should be some-

what less than the part immersed. With all earlier forms of apparatus the dominant source of error was due to superheating of the liquid. The apparatus now described reduces this error to proportions insignificant beside those due to variations in atmospheric pressure during determinations and imperfections of the thermometer.

G. C. J.



Modification of Victor Meyer's Vapour Density Apparatus. G. Romeo. (*Gazz. Chim. Ital.*, 1919, 49, 172-174.)—The principal drawback to Victor Meyer's original apparatus for determining vapour densities is the length of the tube, which makes it inconvenient to work with, and leads to the condensation of part of the vaporised substance in the upper part of the apparatus. This is obviated in the modification here shown, in which the tube *A*, into which the substance is introduced, has a length of only 17 cms., whilst the tube conveying the vapour to the measuring cylinder is formed into a spiral. The conical glass stopper *D*, from the interior of which the air has been exhausted, is ground into the introduction tube *A*, and reaches to the point where the vapours in the exterior tube *L* would come in contact with that tube. The total height of the apparatus is about 40 cms., or half that of the ordinary Meyer apparatus. C. A. M.

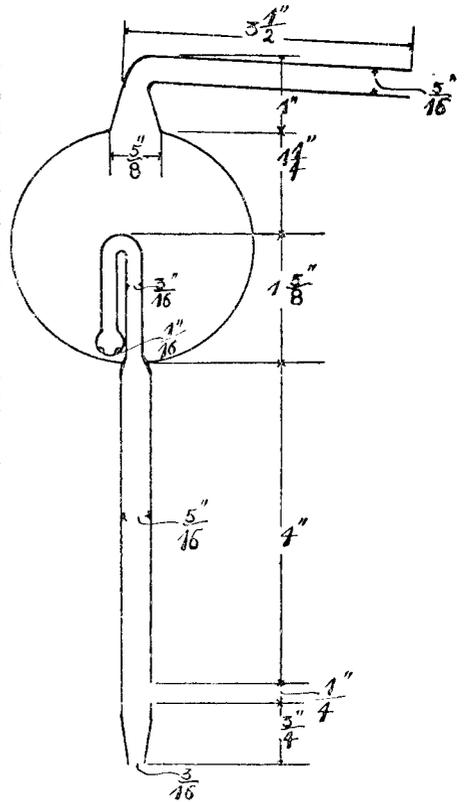
Accuracy of Different Methods of Measuring Small Volumes of Fluid. F. W. Andrews. (*Biochem J.*, 1919, 13, 37-44.)—Experimental evidence in considerable detail is adduced to show the greater accuracy obtainable when measuring small volumes by using the drop method in preference to the pipette method for making accurate dilutions in serological work. Tables are included showing: (1) errors in measurements with small graduated pipettes; (2) deviations from accuracy in a series of dilutions; (3) cumulative error arising from the incorrect use of pipette; (4) cumulative error arising from erroneous technique; and (5) error obtained by the drop method.

Volumes of 1 c.c. and 0.5 c.c. can be measured by pipette with reasonable accuracy. The error attendant on the attempt to deliver 0.1 c.c. may amount to 5 per cent., even when a 0.1 c.c. pipette is employed. The delivery of 0.01 c.c. from

a pipette may be exceedingly inaccurate. The only way in which really accurate results can be obtained with a pipette in preparing an ascending series of dilutions is to use it as a delivery pipette and to wash and dry it out between successive measurements. The alternative method—that of using it as a delivery pipette, mixing the dilution by shaking, and then washing out two or three times with the mixture, rejecting the washings—is one hardly adapted for serological work. Unless such precautions are taken the small error introduced—perhaps only one of 0.5 per cent. in a single measurement, though probably much more with a capillary pipette—becomes magnified into one of 10 per cent. or more at the eighth dilution (see Donald, *Lancet*, 1915, ii. 1243; 1916, ii. 423).
 H. F. E. H.

Scrubber for Ammonia Distillations.

B. S. Davisson. (*J. Ind. and Eng. Chem.*, 1919, 5, 465-466.)—The two principal errors encountered in ammonia distillations arise from the possibility of carrying over alkali and that derived from the use of soft glass. The apparatus described meets both these difficulties, the first by the form of trap used (see Fig.), the large bulb of which has a capacity of 200 c.c., and the second by the adoption of Pyrex glass. The small bulb on the outlet tube has three openings in the same horizontal plane. The first steam which passes into the scrubber condenses on the surface and flows down round the small bulb, where it acts as a scrubbing solution for the remaining vapours, and is then subjected to a long period of steam distillation. The error arising from the solubility of soft glass amounts on the average to about 0.09, grm. of nitrogen, while the combined error of soft glass and entrained alkali is about 0.216 mgrm. of nitrogen. The apparatus described reduces this combined error to an amount approximately the same as that found for titration alone—viz., 0.02 c.c. of $\frac{N}{50}$ acid or 0.005 mgrm. of nitrogen.
 H. F. E. H.



REVIEW

EVERYMAN'S CHEMISTRY. By ELLWOOD HENDRICK. Pp. 319 + x. University of London Press, Ltd., 1918. Price 8s. 6d. net.

The purpose with which this book has been written is wholly admirable, being, in the author's words, to provide the average man with a work which he can read and understand easily, and from which at the same time he can get a chemical view of things. Whether this purpose is possible of achievement is a problem complicated by the difficulty which anyone must have in trying to get a chemical view of things without any laboratory association with chemical substances; moreover, if he once gets a chemical view of things, has he not ceased to be an average man?

Such considerations, however, do not qualify Mr. Hendrick's gallant and genial optimism, in the exercise of which, coupled with unflinching humour, he has produced a very remarkable book, commending itself to the general public and to chemists in equal measure. His method is to engage the reader in a cheery and intimate conversation, in the course of which he brings out all sorts of unsuspected points of contact between everyday life and the facts or principles of chemical science. Some of the sub-headings of his chapters will indicate the plan, beginning with "The Troubles of Neighbour Robinson," through "Faith and the Dream-boy," "The Lean Man and the Fat One," "The Young Devil and the Old Man with a Past," "The Old Horse of Chemistry," "The Ironmaster's Torment, and Why he Swears," "The Righteous Wrath of Neighbouring Farmers," "A Lopsided Leather Test with Policemen and Letter-carriers," and "All Gold does not Glitter," down to "Good-bye." With bluff American hospitality the door of chemistry is thrown open, the reader invited to "step right in," and having done so, is led at once to feel that matter has personality. Then does his buoyant host trot out the animals (disguised as elements and compounds) to perform their tricks, and they do certainly skip and gambol like young lambs at play.

I wish that Mr. Hendrick had been one of my professors, because he has such a way with him, and his explanations of principles are so lucid, whether he is telling of Boyle's Law, of permutit, or of the changes which lead to the loaf of bread. Listen to some of his epigrams: "Nitrogen is the liveliest widower of all the elements;" "the Latin expression for iron is used because you can't make an adjective very well out of iron without the use of *ironic*, which is already pre-empted by literature;" "nitrogen has no chemical conscience whatever;" "fluorine is the young devil, and iodine is the old man with a past;" "the main business of sulphuric acid is to bite into things chemically, and play hobs generally, under control;" "oxygen is certainly a royal and imperial personage among the elements;" "it is a safe rule never to bet on what ammonia will do in a given situation—unless you happen to know;" "if the elements had consciousness, tin would need a group of eminent counsel to defend it from charges of irregularity;" "truth is relative, so are acids and bases;" "carbon disulphide smells like a good old orthodox idea of the Judgment Day."

Detached from their context, these thumb-nail sketches may to some appear frivolous, but they and very many more are just mustard and salt and pepper used to savour the chemical information which the humane Mr. Hendrick knows perfectly well would otherwise be indigestible—to the average man. M. O. FORSTER.



Thomas Fairley.