

THE ANALYST.

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

ORDINARY MEETING, APRIL 14, 1920.

HELD at the Chemical Society's Rooms, Burlington House, Mr. Alfred Smetham, President, in the chair.

Certificates were read for the first time in favour of Misses Dorothy Gertrude Hewer, B.Sc. (London), Rita Catherine Hawkins Johnson, and Messrs. Harold Hall, F.I.C., Geoffrey Trelawney Bray, A.I.C., Frank William George King, and John Robert Stubbs, M.Sc. (Victoria), F.I.C.

A Certificate was read for the second time in favour of Mr. Laurence Harry Mills, B.Sc. (Birmingham), A.I.C.

The following were elected Members of the Society: Messrs. John Carmichael, F.I.C., Herbert John Evans, B.Sc., F.I.C., Cornelius Durham Garbutt, Douglas Henville, F.I.C., Maurice S. Hutchinson, B.Sc., Benjamin Richards James, F.I.C., Geoffrey Martin, D.Sc., Ph.D., F.I.C., Robert Leitch Morris, F.I.C., and James Wood, M.A., B.Sc., F.I.C.

The following papers were read: "The Turbidity Temperature of Fats, Oils, and Fatty Acids: Part I," by Albert E. Parkes, F.I.C.; "The Interpretation of Milk Records," by G. W. Monier-Williams, M.A., Ph.D., F.I.C.; "The Loss of Free Ammonia from Drinking Water Samples," by A. F. Joseph, D.Sc., F.I.C., and G. A. Freak, B.Sc., F.I.C.; and "A Decanting and Filter Washing Machine," by Eric Sinkinson, A.I.C.

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A NEW METHOD FOR THE ESTIMATION OF METHYL ALCOHOL.

BY S. B. SCHRYVER AND CYRIL CHRISTIAN WOOD.

A. Estimation of Methyl Alcohol in Water.

SOME years ago, one of the authors described a method for the detection of formaldehyde, which could be applied to the quantitative estimation of very small amounts of this substance (*Proc. Roy. Soc.*, 1910, B. **82**, 226, and reports of Inspector of Foods, Local Government Board, 1909, N. S. No. 12, also *ANALYST*, 1909, **34**, 470). The method in question consisted in treating the solution containing the formaldehyde with 1 per cent. solution of phenylhydrazine hydrochloride, then adding potassium ferricyanide, and afterwards concentrated hydrochloric acid, when, in the presence of the aldehyde, a brilliant fuchsine-like colour was produced, which could be detected even when the concentration of formaldehyde did not exceed 1 in 2,000,000. This reaction forms the basis of the method for estimating methyl alcohol described in the present communication.

Several reagents are capable of oxidising methyl alcohol to formaldehyde, but most of these interfere with the application of the test described above. This was not found, however, to be the case when ammonium persulphate was used. If an excess of the persulphate is added, the formaldehyde is oxidised further to carbon dioxide and water. By ascertaining the amount of persulphate that must be added to a given solution of methyl alcohol in water, so that after completion of the reactions under certain standard conditions of experiment formaldehyde just fails to be detectable by the above-mentioned reaction, the percentage of the alcohol present in the water can be estimated with a considerable degree of accuracy, even when the amounts present are as low as 0.0005 per cent.

When ammonium persulphate is heated with a solution of methyl alcohol three reactions can take place simultaneously—viz., the decomposition of the persulphate itself, the oxidation of methyl alcohol to formaldehyde, and the oxidation of the aldehyde. It is, therefore, necessary to specify accurately the conditions under which the estimation should be carried out, as is the case in other oxidation methods, such as that of Fehling's, where several oxidation processes take place at the same time.

The method of carrying out the estimation is as follows: Samples, each of 5 c.c. of the methyl alcohol solution in water are introduced into a series of test tubes (6 inches by $\frac{3}{4}$ inch), and mixed with 5 c.c. of ammonium persulphate solution of varying concentrations. The test-tubes containing these mixtures are then inserted into a water bath containing boiling water, in which they are kept immersed for 10 minutes. At the end of this period 1 c.c. of the mixture is pipetted out from each tube and introduced into a series of smaller test-tubes, each of which contains 1 c.c. of a 1 per cent. solution of phenylhydrazine hydrochloride; to these mixtures are then added 1 c.c. of a 2.5 per cent. solution of potassium ferricyanide and about 3 c.c. of concentrated hydrochloric acid. It will be found

from this preliminary series of experiments that the concentration of methyl alcohol will lie between two limits—viz., a higher limit corresponding to a concentration of the persulphate which is sufficient to oxidise completely the formaldehyde formed in the reaction, and a lower limit in which the concentration is insufficient, and the mixture of persulphate and methyl alcohol solution still gives a positive reaction for formaldehyde after heating for ten minutes. A second series of experiments can then

TABLE I.

Per Cent. Persulphate in 5 c.c. used for Oxidation.	Per Cent. of Solution of MeOH used.	C.c. of this Solution in 10 c.c. Mixture.	Formaldehyde Reaction.	Concentration of MeOH in 5 c.c. Aqueous Solution.
5.0 5.0	1.0 1.0	1.45 1.40	+ 0	0.29 0.28
4.0 4.0	0.5 0.5	2.4 2.3	+ 0	0.24 0.23
3.0 3.0	0.25 0.25	3.45 3.40	+ 0	0.1725 0.170
2.0 2.0	0.25 0.25	2.3 2.25	+ 0	0.115 0.1125
1.0 1.0	0.1 0.1	2.8 2.7	+ 0	0.056 0.054
0.5 0.5	0.1 0.1	1.5 1.4	+ 0	0.030 0.028
0.25 0.25	0.05 0.05	1.5 1.4	+ 0	0.015 0.014
0.10 0.10	0.025 0.025	1.0 0.9	+ 0	0.0050 0.0045
0.05 0.05	0.010 0.010	1.3 1.2	+ 0	0.0026 0.0024
0.025 0.025	0.005 0.005	1.3 1.2	+ 0	0.0013 0.0012
0.010 0.010	0.001 0.001	2.5 2.4	+ 0	0.00050 0.00048

be carried out in a similar manner to the first, mixing 5 c.c. of the methyl alcohol solution with 5 c.c. of persulphate in concentrations varying only between the two above-mentioned limits. The number of mixtures in this series can be varied according to the degree of accuracy which is desired in the estimations. If, for example, it was found that the mixture of 5 c.c. methyl alcohol solution mixed with 5 c.c. of 4 per cent. persulphate gave a negative reaction for formaldehyde in the first series of experiments, whilst the solution mixed with 5 c.c. of a 3 per cent. solution gave a positive reaction, in the second series of experiments the methyl alcohol solution was mixed with ammonium persulphate solutions varying only between 3 and 4 per cent. For each concentration of methyl alcohol, therefore, there corresponds a definite concentration of the persulphate which is just sufficient, under the specified conditions of experiment, to oxidise all the formaldehyde which is formed in the reaction.

In the table on p. 165 are given the concentrations of methyl alcohol which are completely oxidised (so as to give a negative formaldehyde reaction) by concentrations of persulphate varying from 0.001 to 5 per cent.

The above table represents the final results of a detailed series of experiments, of which one is given *in extenso* to illustrate more clearly the method employed.

To determine the concentration of the solution of methyl alcohol which is just oxidised by a 5 per cent. persulphate solution, so that no formaldehyde is present after heating the mixture for ten minutes :

<i>First Series :</i>		Reaction (Formaldehyde).	
5 c.c. of this 5 per cent. persulphate solution +			
5 c.c. of 1 per cent. solution of methyl alcohol	strong pink
4 c.c. " " "	1 c.c. H ₂ O	...	pink
3 c.c. " " "	2 c.c. H ₂ O	...	"
2 c.c. " " "	3 c.c. H ₂ O	...	"
1 c.c. " " "	4 c.c. H ₂ O	...	0

Hence the concentration of methyl alcohol solution, 5 c.c. of which is completely oxidised by 5 per cent. persulphate, lies between $\frac{1}{3}$ and $\frac{2}{5}$ of 1 per cent.

To determine the concentration more accurately, the following second series of experiments was carried out :

5 c.c. persulphate solution +		Reaction (Formaldehyde).	
1.5 c.c. of 1 per cent. solution of methyl alcohol	3.5 c.c. H ₂ O	...	faint pink
1.45 c.c. " " "	3.55 c.c. H ₂ O	...	just pink
1.4 c.c. " " "	3.6 c.c. H ₂ O	...	0
1.3 c.c. " " "	3.7 c.c. H ₂ O	...	0
1.2 c.c. " " "	3.8 c.c. H ₂ O	...	0
1.1 c.c. " " "	3.9 c.c. H ₂ O	...	0

Thus if the end point is taken to be that concentration which just gives the pink formaldehyde reaction after heating for ten minutes with the persulphate solution, it will be found that 5 per cent. of the latter just oxidises 5 c.c. of a solution containing

$\frac{1.45}{5} \times 1$ per cent. = 0.29 per cent. methyl alcohol. The percentages of methyl

alcohol corresponding to the various concentrations of persulphate are given in the final column of Table I. It is obvious that the concentration of a persulphate solution just necessary to oxidise a given concentration of methyl alcohol is a linear function of that concentration, and if c be the concentration (per cent.) of the persulphate, x that of the methyl alcohol, and k a constant, then $x = kc$. If this be calculated from the above table (neglecting the data for percentages of persulphate below 0.25 per cent.) k will be found to be = 0.059. These data were obtained with a methyl alcohol sample which had the correct boiling point, after careful fractionation over lime, and with a sample of persulphate in which the amount of ammonium persulphate was estimated by warming with a definite amount of standardised ferrous sulphate solution and determining the amount of the latter oxidised by titration against permanganate solution; this sample was found to contain 98.6 per cent. ammonium persulphate. In a series of experiments carried out with another sample of persulphate which was less pure, the constant k was found to be 0.054. In carrying out the estimation of methyl alcohol by the method above described, with any given sample of persulphate, it is best to standardise 5, 4, or 3 per cent. solutions against methyl alcohol and to determine directly the constant k . Only a few experiments will be necessary, as the results will only differ slightly (by fractions of a c.c.) from the numbers given in Table I., column 3.

B. Estimation of Methyl Alcohol in Ethyl Alcohol.

An attempt was made to estimate methyl alcohol in ethyl alcohol by the same method as that employed for estimating the methyl alcohol in water. This was found, however, to be impracticable, and there is no preferential oxidation of the lower alcohol by persulphate. It was found, for example, that the amounts of the latter necessary to oxidise to the end point (disappearance of formaldehyde) did not differ, outside the limits of experimental error, with ethyl alcohol mixtures containing 4 and 5 per cent. of methyl alcohol. Another method had therefore to be employed. This consisted in treating a persulphate solution with an excess of the mixture of alcohols, and examining the products produced in the initial stages of oxidation. It was then found that, under conditions such as these, the larger the amount of methyl alcohol present, the greater the amount of formaldehyde present, when the limited amount of persulphate used was entirely decomposed. The amount of formaldehyde produced under the conditions of the experiment could then be estimated colorimetrically. The estimations were carried out as follows: Ten c.c. of the ethyl alcohol containing methyl alcohol are diluted with 50 c.c. of water. Five c.c. of this are then mixed with 5 c.c. of a 1 per cent. solution of ammonium persulphate in a test-tube; this is provided with a short air condenser and heated in a boiling water-bath for ten minutes. At the end of this period, 1 c.c. of the mixture is added to 1 c.c. of a 1 per cent. solution of phenyl hydrazine hydrochloride, *with which it is heated in a boiling water-bath for five minutes*. After cooling, 1 c.c. of a 2.5 per cent. solution of potassium ferricyanide is added, and then 3 c.c. of concentrated hydrochloric acid. A pink colour is thereby produced when methyl alcohol is present, which can be compared with the colours produced in a similar way from samples of

ethyl alcohol containing known amounts of methyl alcohol. Experiments have been carried out with mixtures of ethyl alcohol and methyl alcohol, when the latter varied from 0.5 to 5 per cent., and it is possible by this rough comparison to estimate the percentage of methyl alcohol when contained within these limits to within 1 per cent. A more accurate estimation can be obtained when a colorimeter is employed. The method of carrying out the more accurate determination is described below.

It will be noticed, in the directions given above, that the reaction mixture is heated with the solution of phenylhydrazine hydrochloride before the other reagents are added, when carrying out the test for formaldehyde. The reason of this is that during the reaction certain quantities of the ethylal $\text{HCH}(\text{OC}_2\text{H}_5)_2$, and probably of the methylal $\text{HCH}(\text{OCH}_3)_2$, are formed during the heating, and the full pink colour is not given by formaldehyde combined in these ways, unless the mixture is heated with the solution of phenyl hydrazine hydrochloride before adding the other reagents. (Compare Schryver *loc. cit.*)

In carrying out the more accurate colorimetric estimations, the pink test solutions prepared by the method described above were diluted with 70 c.c. of water, and the colour was then compared with a standard prepared in an exactly similar way from a sample of ethyl alcohol containing a known amount of methyl alcohol. When a colorimeter of Schmidt and Haensch was used, differences could be detected between samples of ethyl-methyl alcohol mixtures in which the amounts of methyl alcohol differed by only 0.2 per cent. Possibly, with a more modern form of colorimeter, more accurate estimations would be possible. The researches on the determination of the amounts of methyl alcohol in ethyl alcohol have, up to the present, been confined to mixtures containing between 0.5 and 5 per cent. of the former.

The sample of ethyl alcohol gave a faint formaldehyde reaction when oxidised, and the oxidation products were tested for methyl alcohol in the manner described above. Whether this is due to the fact that it contains small amounts of the lower alcohol, or to the fact that formaldehyde is formed in small amounts by the oxidation of ethyl alcohol, it is impossible at the present to say.

C. Estimation of Methyl Alcohol in Acetone.

It was found that a similar method could be applied to the estimation of methyl alcohol in acetone to that employed for estimating this alcohol in water, as the acetone is only oxidised to a slight extent by persulphate. In the former case, however, there were certain difficulties in carrying out the estimation, which have necessitated, when the percentage of methyl alcohol present is small, certain minor modifications in the process. It was found when the acetone contained 4 per cent. or more of methyl alcohol that, as a certain concentration of persulphate was exceeded, there was a sudden transition from the bright pink colour yielded by the formaldehyde test to a light pink, and this latter colour persisted even when the above-mentioned concentration of persulphate was considerably above this transition point. This phenomenon is probably due to the formation of a condensation product of formaldehyde with acetone, which is very resistant to oxidation by persulphate. When the amount of methyl alcohol in acetone falls below 4 per cent., the transition

point is not very marked. At 4 per cent. and over, when higher concentrations of persulphate must be used, the point is unmistakable; for each given concentration of methyl alcohol in acetone, under the conditions of experiment described below, there corresponds a given concentration of persulphate, a small addition to which causes a sudden transition from a bright pink to a light pink, when the formaldehyde test is applied. By this method it is easy to determine to within 0.2 per cent. the percentage of methyl alcohol in acetone when the former varies between 4 and 20 per cent. (above the latter limit no experiments were carried out). When the percentage is below the former limit it can be determined approximately by comparing the colour reactions with those produced by acetone containing known amounts of methyl alcohol and when the experiments are carried out under the same conditions.

As an alternative method, when results accurate to within 0.2 per cent. can be obtained, the acetone mixture containing the lower percentage of methyl alcohol can be mixed with one containing a known higher percentage, so as to bring the total in the mixture to more than 4 per cent., and then carrying out the estimation of the methyl alcohol in this mixture by the method described in detail below, subsequently deducting the amount of added methyl alcohol from the result. A convenient method of carrying out the process is to add to the acetone-methyl alcohol mixture (containing the unknown amount of methyl alcohol) an equal volume of acetone containing 10 per cent. (by volume, as the specific gravities of methyl alcohol and acetone differ only very slightly) of methyl alcohol. By subtracting 5 from the percentage found in this mixture, and doubling the number thus obtained, the percentage of methyl alcohol in the mixture under investigation can be calculated.

The actual determination was carried out in the following manner: 5 c.c. of the acetone containing methyl alcohol under investigation were diluted to 250 c.c. with

TABLE II.

Per Cent. MeOH in Methyl-Alcohol Acetone Mixture.	Formaldehyde Reaction after Heating with Persulphate Solutions of the following Concentrations—				
	5 Per Cent.	4 Per Cent.	3 Per Cent.	2 Per Cent.	1 Per Cent.
10	0	?	+++	+++++	+++++
9	0	?	+++	+++++	+++++
8	0	0	+	+++	+++++
7	0	0	?	+++	+++++
6	0	0	0	++	+++++
5	0	0	0	+	+++++
4	0	0	0	?	+++
3	0	0	0	0	+++
2	0	0	0	0	+
1	0	0	0	0	?

water. Quantities each of 5 c.c. of this mixture were introduced into a series of test-tubes ($6'' \times \frac{3}{4}''$) containing 5 c.c. of ammonium persulphate solutions of varying concentrations. The test-tubes were provided with corks containing short air-condensers, and were then introduced into a water-bath containing boiling water in which they were kept immersed for ten minutes. At the end of this period each mixture was shaken, and the formaldehyde test was applied (using 1 c.c. of the hot solution) in the manner already given under the description of the determination of methyl alcohol in water. By using persulphate solutions of 1, 2, 3, 4, 5 per cent., an approximate estimation of the methyl alcohol can be made, as will be obvious from the table given on p. 169.

In the following table are given the percentages of persulphate in 5 c.c., which, when mixed with 5 c.c. of the diluted methyl alcohol acetone mixtures, just gave the positive reaction described above, which corresponds to the end point.

TABLE III.

Per Cent. CH_3OH in Original Mixture.	Per Cent. Concentration of Persulphate in 5 c.c. added.	Per Cent. CH_3OH in Original Mixture.	Per Cent. Concentration of Persulphate in 5 c.c. added.
20.0	6.4	8	2.56
17.5	5.8	7	2.24
15.0	4.8	6	2.04
12.5	4.0	5	1.7
10.0	3.2	[4	1.45]
9.0	2.9	—	—

The above researches were carried out for the Food Investigation Board.

Conclusions.—(1) A method for estimation of methyl alcohol in water is described, the essential principle of which consists in determining the concentration of ammonium persulphate necessary to destroy completely the formaldehyde formed in the initial stages of the oxidation process under certain specified conditions of experiment. For the detection of formaldehyde, the method previously described by one of the authors has been employed.

(2) By a slight modification of this method the amount of methyl alcohol in acetone can be estimated.

(3) To determine the amount of methyl alcohol in ethyl alcohol, the mixture of alcohols is partially oxidised by a relatively small amount of persulphate (the alcohols being in excess), and the formaldehyde formed under these conditions is estimated colorimetrically.



NOTE ON OPIUM POISONING.

By E. H. HANKIN, M.A., D.Sc., AND D. CHATTERJI.

DURING the last three years stomachs, with their contents, of fifty-three persons have been examined in this laboratory, in which the history of symptoms and other evidence obtained by the police indicated that opium was the cause of death.

The results of analysis were as follows: In one case no opium was detected, but opium was found in the viscera of another person who had been poisoned at the same time; in four cases the results of analysis were consistent with the presence of traces of opium; in twenty cases traces only of opium were detected; in nine cases opium was detected in small quantity; in ten cases opium was detected in medium quantity; in nine cases opium was detected in quantity.

By the term "small quantity" we mean that the residue obtained from a Stas-Otto extract gave colour reactions about as strongly as would the Stas-Otto extract of 7 mgrms. of Indian opium of 2 per cent. morphine content. The term "medium quantity" similarly corresponds to about 15 mgrms., and "detected in quantity" corresponds to 20 or more mgrms.

Thus there was a clearly negative result in one case. Out of the remaining fifty-two cases, in twenty-four opium was either detected in traces or the tests were responded to so faintly that no definite statement could be made as to the absence or presence of the poison. That in such a large proportion of the cases opium should only be detected in traces appears to be in accord with results obtained by other observers (see Witthaus, *Manual of Toxicology*, second edition, p. 980).

The only tests we have found to be of use in testing for opium in viscera are the following:

(1) *The Porphyroxin Test.*—We have carried out this test on several thousand extracts of viscera and other substances without ever getting a well-marked reaction, except in cases in which it was probable, on other grounds, that opium was present. On the other hand, a faint pinkish colour occurs not infrequently in the absence of opium.

(2) *The Husemann Reaction.*

(3) *The Urotropin or Formaldehyde Reaction.*

The last-mentioned test has been used as a colorimetric test for morphine in viscera (ANALYST, 1917, 42, 227). But, in our experience, there are grounds for doubting whether either this test or any other known to us can be depended on to give a reliable colorimetric result. The viscera are always sent to us preserved in alcohol. In the hot Indian climate it often happens that much decomposition has set in before the viscera are placed in alcohol. With such viscera we find that if an extract responds strongly to one of the above three tests there is no certainty that it will respond strongly to the others. The extent of this discrepancy is shown by the following table. It refers to analyses of thirty-one stomachs, three specimens of vomit, one of liver, and one of urine, a total of thirty-six specimens. In each case the history of symptoms, etc., had pointed to opium poisoning:

Reaction given by the—		Reactions given in the same cases by—	
Urotropin Test.		Porphyroxin Test.	Husemann Test.
Strong in eight cases ...	Strong	2	7
	Medium	5	0
	Negative or doubtful	1	1
Medium in sixteen cases	Strong	4	3
	Medium	12	13
	Negative or doubtful	0	0
Doubtful in six cases ...	Strong	0	1
	Medium	5	4
	Negative or doubtful	1	1
Negative in six cases ...	Strong	0	0
	Medium	6	6
	Negative or doubtful	0	0

Thus, in eight cases in which the urotropin reaction was strong, the porphyroxin reaction was only given strongly in two. In six cases the urotropin test gave a negative result, and in each of these the extract reacted with medium strength to the porphyroxin and Husemann tests. There can be little doubt that the cause of the occasional failure of the urotropin test is the inevitable presence of impurities in the extracts. It appears to be particularly difficult to get a pure extract in cases of opium poisoning. If an extract has a yellowish colour there is a presumption, in our experience, that it is going to respond strongly to the tests for opium.

When dealing with highly decomposed viscera preserved for a fortnight or more in alcohol, no amount of washing with ether or with ether and chloroform will so purify the acid solution that it will not allow impurities to pass into the solvent when made alkaline. Repeated washing of the acid solution with ether is likely to result in the porphyroxin test yielding a negative result, and a valuable piece of evidence will thus be lost. Hence, in carrying out the Stas-Otto process, we wash the acid solution once only with ether. The solution is then made alkaline and extracted with ether and chloroform. It is advisable to add these solvents separately. One part of chloroform is first added, then about three parts of ether, then a piece of litmus paper and, lastly, a few drops of ammonia. The mixture is then immediately shaken. We find that chloroform and ether thus used yield a purer extract than either an ethyl acetate-ether mixture or amyl alcohol.

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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.

DETECTION OF COAL-TAR DYES IN BUTTER AND MARGARINE.

THE presence of these dyes can be readily detected by the fact that they are more stable to heat than vegetable butter-dyes or the natural colouring matter in butter.

The author has found on heating the clear filtered fat from butter or margarine to a temperature of 180° to 190° C. that natural butter colour and vegetable colours are destroyed, whilst coal-tar colours are not.

The test is carried out as follows: About 1 c.c. of the clear filtered fat (this is separated at a temperature not above 100° C.) is placed in a test-tube and immersed in an oil-bath which is raised to about 185° C. The test-tube is removed occasionally, shaken and replaced. In the absence of coal-tar dye the fat will become colourless within ten minutes; if the fat remains coloured, then coal-tar dye is present.

It has been found that butter-fat separated at temperatures above 100° C. will not become colourless on heating.

G. VAN B. GILMOUR.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Modification of the American Official Chlorine Method for Feeds, Faeces, and Urine. J. O. Halverson and E. B. Wells. (*J. Biol. Chem.*, 1920, **41**, 205-208.)
—Reasons are given for the inconsistent results obtained by the use of the official Volhard method, and the following modification is described. The alkaline ash is digested with dilute nitric acid, filtered and washed with hot water, the total volume of filtrate not exceeding 75 c.c. This solution is then boiled, $\frac{N}{10}$ silver nitrate gradually added in excess, and the boiling continued until the volume is reduced to 25 or 30 c.c. When cold, the solution is transferred to a 100 c.c. flask, made up to the mark, mixed, and, after standing for three hours, is filtered. Ninety-five c.c. are measured by a pipette, 2 c.c. of ferric nitrate indicator (prepared by boiling 125 c.c. concentrated nitric acid with 325 c.c. water until colourless, and adding 50 c.c. of saturated ferric nitrate solution) added and titrated with $\frac{N}{40}$ ammonium thiocyanate, using a burette capable of being read to 0.01 c.c. A table is given showing results obtained on corresponding samples by the above, and by the official method, indicating that the former yields slightly higher (0.4 to 3 per cent.) values. Tests

made on salts of known chlorine content show that the proposed method yields a maximum error of ± 0.7 per cent., whilst the official method gives deviations of from 1 to 2 per cent.

T. J. W.

Identification of Citric Acid in the Tomato. R. E. Kremers and J. A. Hall. (*J. Biol. Chem.*, 1920, **41**, 15-17.)—Strained tomato-pulp was saturated with calcium hydroxide and the calcium citrate obtained precipitated by boiling. The precipitate is not the pure calcium salt, since this requires 21.4 per cent. of calcium and only 15.6 per cent. was found. This impure calcium salt does not yield crystals when brought into reaction with phenacyl bromide; its purification is effected by conversion into the sodium salt with boiling sodium carbonate, and the calcium citrate is then re-precipitated by adding ammonium chloride and calcium chloride in excess to the solution of the sodium salt, followed by boiling and filtering whilst hot. The calcium salt is dissolved in 50 per cent. acetic acid, from which solution the lead salt is precipitated by basic lead acetate, the lead salt being then decomposed with sulphuretted hydrogen. The citric acid solution is filtered from the lead sulphide, concentrated in vacuo and crystallised in a vacuum desiccator. The triphenacyl ester was then prepared as follows: 0.7382 gm. of citric acid dissolved in 9 c.c. of water was neutralised with 0.5389 gm. of sodium carbonate; 1.61 gm. of phenacyl bromide dissolved in 18 c.c. of alcohol were added, and the mixture was boiled under a reflux for three hours. The reaction mixture was crystallised, the yield was 0.52 gm., melting at 104 to 105° C. Mixed with ester from U.S.P. sodium citrate, the m.-pt. was 104 to 105° C. Therefore, the presence of citric acid in the tomato juice has been shown by means of its triphenacyl ester.

H. F. E. H.

Estimation of Crude Fibre. O. Nolte. (*Zeitsch. anal. Chem.*, 1919, **58**, 392-397.)—In the case of soft substances, the fineness of the powder has but little effect on the quantity of crude fibre obtained by the usual method of analysis; but with hard substances, such as buckwheat shells, barley chaff, etc., the coarse powder (larger than 2 mm.) yields about 4 to 5 per cent. more crude fibre than does the finely powdered material. Removal of fat before the acid and alkali treatment is unnecessary even in the case of fatty materials such as rape seed.

W. P. S.

Yield of Hydrocyanic Acid by *Phaseolus lunatus* Beans. H. Lührig. (*Chem. Zeit.*, 1920, **44**, 166-167.)—The quantity of hydrocyanic acid found in nine samples of *Phaseolus lunatus* beans varied from 5.1 to 23.4 mgrms. per 100 grms. of beans. Treatment of the bean mash with emulsin did not materially increase the yield of hydrocyanic acid. The beans, after they had been steeped in water and then boiled for three hours, were free from bitter taste and did not produce any injurious effect when eaten in considerable quantity. (Compare also ANALYST, 1917, **42**, 174.)

W. P. S.

Detection of Invertase in Honey. A. Caillas. (*Comptes rend.*, 1920, **170**, 589-592.)—By precipitation with alcohol the author has separated from honey a substance which, by its action on cane sugar, was proved to be invertase; the yield was

0.049 per cent. of the honey. The presence of invertase in honey would explain the gradual disappearance of the cane sugar in honey when the latter is kept for some considerable time.

W. P. S.

Sugar in Oat Straw and Cattle Foods. S. H. Collins and A. Spiller. (*J. Soc. Chem. Ind.*, 1920, 39, 66T.)—Many of the commoner cattle foods naturally contain sugar which is valuable in making them more palatable. The superiority of early-cut over late-cut oat straw probably depends on the higher sugar content of the former; by fermentation, however, much of the sugar may be lost by conversion into alcohol, lactic acid and butyric acid. Earth nut cake contains as much as 8.46 per cent. of sugar, all non-reducing. The total sugar in oat straw cut early ranges from 5.00 to 6.47 per cent., most of it being in the form of invert sugar. This sugar decreases considerably on storage, and in some cases disappears altogether. For the estimation, 5 grms. of the fodder are extracted with ether, and treated with 5 grms. of lead acetate and 250 c.c. of water. The mixture is allowed to stand overnight, then filtered, and 50 c.c. of the filtrate are acidified with 5 c.c. of strong hydrochloric acid, and warmed slowly so that it reaches 60° C. after twenty minutes. Any lead chloride is filtered off, dry sodium carbonate is added in excess, and the filtered liquid titrated with Fehling's solution. Some difficulty is experienced in obtaining clear solutions, and the cuprous oxide tends to remain persistently in suspension.

J. F. B.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Detection and Characterisation of Dextrose in Plants by a New Biochemical Method. E. Bourquelot and M. Bridel. (*Compt. rend.*, 1920, 170, 631-635.)—The ordinary methods of identification, namely reduction of Fehling's solution, fermentation by yeast and the formation of glucosazone, are not sufficient for the definite characterisation of dextrose, since other monose sugars possess the same properties. The authors describe a method for the identification of dextrose which is perfectly specific. This test consists of a reversal of the method for the detection of glucosides by emulsin. The hydrolytic action of emulsin is reversible, and if this enzyme be added to a solution of dextrose in an alcohol a glucoside is produced and the optical activity of the liquid becomes levorotatory in proportion to the quantity of glucoside formed. The reaction has been demonstrated in the following manner: A solution is made in 70 per cent. methyl alcohol of 2.0565 grms. of dextrose per 100 c.c. The rotation of this solution in the 200 mm. tube is +2° 20'. To this is added 0.5 gm. of emulsin, and the mixture is allowed to stand at the temperature of the laboratory. At the equilibrium point the rotation will be found to have become -50' corresponding to a displacement to the left of 3° 10', from which it is calculated that 1.6978 grms. or 82.55 per cent. of the dextrose has combined with the alcohol. Moreover, the methylglucoside is easily isolated by evaporating the solution to dryness under reduced pressure and extracting the residue with boiling ethylacetate, from which the glucoside crystallises on cooling. Further experiments with mixtures of dextrose with mannose, fructose, and arabinose showed that only the

dextrose was etherified, and, under the conditions above mentioned, 83 per cent. of the dextrose was always combined. The specific rotatory power of β -methylglucoside is -32.5° . The method has been applied for the identification of dextrose in juniper berries and in the glucoside loroglossin obtained from *Loroglossum hircinum* Rich.

J. F. B.

Comparative Study of Hæmoglobin Determination by Various Methods.

F. S. Robscheit. (*J. Biol. Chem.*, 1920, **41**, 209-226.)—The history of various methods of hæmoglobin determination is given, their disadvantages indicated, and tables showing comparative results obtained by the different methods are provided. A modification is described, which consists of the application of Palmer's procedure for comparison of the colour of carbon-monoxide hæmoglobin solutions (*J. Biol. Chem.*, 1918, **33**, 119) to Sahli's acid hæmatin method (*Lehrbuch der klin. Untersuchungs-Methoden*, Leipsic, Fourth Edition, 1905). The oxygen capacity of dog's blood is determined by Van Slyke's method (*J. Biol. Chem.*, 1918, **33**, 127), and the hæmoglobin content calculated. A 20 per cent. suspension is prepared, such that a 1 per cent. dilution would read 100 per cent. hæmoglobin. The undiluted standard retains its original colour at least eight months if kept in an ice-chest. One c.c. of this solution is pipetted into about 50 c.c. of $\frac{N}{10}$ hydrochloric acid, mixed, the volume made up to 100 c.c. with $\frac{N}{10}$ hydrochloric acid, and left to stand in an ice-chest for one hour. The flask is then thoroughly shaken and the solution transferred to a colorimeter tube. The blood under examination is treated in the same manner, and the colour compared with the standard. The illuminant may be daylight or a nitrogen-filled electric bulb, fitted with a "Daylite" colour screen. The dilute acid hæmatin solutions slowly fade after about a week, even if kept in an ice-chest. Similar results are obtained whether sheep's, goat's, or human blood be employed as the standard.

T. J. W.

Determination of Methæmoglobin in Blood. **W. C. Stadie.** (*J. Biol. Chem.*, 1920, **41**, 237-241.)—Two c.c. of oxalated whole blood are placed in a 100 c.c. flask, 50 c.c. of water added, and 0.5 c.c. of a 3 per cent. potassium ferricyanide solution is then run in, and the flask allowed to stand about twenty minutes, after which 5 c.c. of a 0.1 per cent. potassium cyanide solution are added, and the mixture made up to 100 c.c. by the addition of water. The colour is then compared with a standard of known strength in a colorimeter, and the result represents the hæmoglobin plus methæmoglobin, which is expressed as grms. of "total hæmoglobin" per 100 c.c. of blood. *Preparation of Standard:* The hæmoglobin content of fresh whole oxalated or defibrinated blood free from methæmoglobin is determined gasometrically, 10 c.c. of the blood are hæmolysed by the addition of about 300 c.c. of water, 2.5 c.c. of the above potassium ferricyanide solution are run in, and, after twenty minutes, 25 c.c. of the potassium cyanide solution are added, and the whole made up to 500 c.c. with water. The actual hæmoglobin present in the sample under examination is determined by aerating 4 to 5 c.c. of the blood in a funnel and determining the total oxygen content by the Van Slyke method. Dividing the figure representing this value by 1.34 gives the grms. of hæmoglobin per 100 c.c. of sample. The

methæmoglobin present is deduced by deducting the actual hæmoglobin content from the "total hæmoglobin." Tables are provided for the correction of gas volumes obtained in the gasometric determination of hæmoglobin, and results of methæmoglobin determinations made by the above method compared with the corresponding calculated values. These show satisfactory agreement. Attempts were made by the author to estimate methæmoglobin by conversion into carbonmonoxide-hæmoglobin; and also into acid hæmatin, but were unsuccessful.

T. J. W.

Estimation of Indole in Biological Media. H. F. Zoller. (*J. Biol. Chem.*, 1920, **41**, 25-36.)—Previous methods devised for the estimation of indole are discussed, and various difficulties met with in their application are pointed out. The present method is based on the results obtained in former work performed by the author upon the distillation of indole (Zoller: *J. Biol. Chem.*, 1920, **41**, 37-44) in combination with a modification of Nonnetta and Demanche's application of Baeyer's nitroso-indole reaction. To 100 c.c. of the medium under examination $\frac{N}{4}$ sodium hydroxide solution is added until the hydrogen ion concentration equals PH. 9.2; this will be attained when a spot test shows a clear red colour with phenolphthaleïn, and no blue colour with thymolphthaleïn, both indicators having a concentration of 0.02 per cent. The solution is then distilled until about 10 c.c. remain, and the distillate is diluted to 100 c.c. A standard solution is prepared by dissolving 10 mgrms. of pure indole in 100 c.c. of water, and varying portions containing 0.02 to 0.20 mgrm. of indole are run into a series of test-tubes uniform in diameter and colour, and each diluted to 10 c.c. To each tube 2 drops of 1 per cent. sodium nitrite solution and 5 drops of concentrated sulphuric acid are added; the contents are then gently mixed and allowed to stand about five minutes. The solution is extracted with three 3 c.c. portions of either isoamyl or isobutyl alcohol, and the coloured alcoholic extracts pipetted into another test-tube, and diluted to exactly 10 c.c. These standards are permanent for at least one week. An aliquot portion of the distillate, containing from 0.01 to 0.20 mgrm. of indole, is transferred to a tube and treated in the same manner as the standard solutions, the indole present being estimated by comparison of the red colour produced with those of the standards. A table is provided, showing that the results obtained by the author's method agree satisfactorily with those yielded by the β -naphtha-quinone-sodium-mono-sulphonate method of Bergeim (*J. Biol. Chem.*, 1917, **32**, 17), while the time occupied by the former determination is less than one-third that required for the latter. The new method is simple, reliable, and rapid, and requires no special apparatus.

T. J. W.

Estimation of Potassium and Sodium in Small Quantities of Blood. B. Kramer. (*J. Biol. Chem.*, 1920, **41**, 263-274.)—*Potassium.*—One c.c. of blood or 3 to 5 c.c. of clear plasma or serum is dried in a platinum dish on a steam bath, and finally at 110° C. for thirty minutes. The residue is gradually heated until completely incinerated, keeping the temperature as low as possible. On cooling, the ash is dissolved in 0.5 c.c. of water with one or two drops of glacial acetic acid and 0.5 to 1.0 c.c. of sodium cobalti-nitrite reagent (see below) are gradually added with stirring and the mixture left for ten minutes. The precipitate is filtered off through

a Gooch crucible provided with a thick asbestos felt, and washed with cold water until the washings are clear. The asbestos and precipitate are transferred to a beaker, 25 c.c. of $\frac{N}{100}$ potassium permanganate and 5 c.c. of 25 per cent. of sulphuric acid added, and the mixture heated on a water-bath for three minutes. Sufficient $\frac{N}{100}$ oxalic acid is run in to decolorise the solution completely, and this is immediately titrated with $\frac{N}{100}$ potassium permanganate to a permanent pink colour. The total volume of the potassium permanganate solution used minus the volume of oxalic acid solution added $\times 0.071 =$ mgrm. of potassium in the sample. Sodium cobalti-nitrite reagent: (A) 50 grms. of cobalt nitrate are dissolved in 100 c.c. of water, and 25 c.c. of glacial acetic acid added (B) 50 grms. of pure sodium nitrite in 100 c.c. of water. Six volumes of A are mixed with ten volumes of B, and air bubbled through the mixture. The mixed reagent will keep for at least a month in an ice-box, and should be filtered before use.

Sodium.—The ash from 1 or 2 c.c. of material obtained as in the potassium estimation is dissolved in 0.5 or 1 c.c. of water and one drop of $\frac{N}{4}$ hydrochloric acid. Fresh 10 per cent. potassium hydroxide solution is added until slightly alkaline, and 15 c.c. of potassium pyroantimoniate reagent (see below) run in followed by one-fifth the total volume of absolute alcohol. The mixture is left to stand at least two hours, transferred to a moist asbestos Gooch filter, washed with 3 c.c. portions of 30 per cent. alcohol, dried at 110° C. and weighed. A blank estimation should always be made. Potassium pyroantimoniate reagent: 2 grms. of the salt are boiled with 100 c.c. of water until no more dissolves, 3 c.c. of 10 per cent. potassium hydroxide are added and the mixture stirred and filtered. This reagent should be freshly made.

The methods are usually accurate to within 3 per cent. The potassium content of normal human serum varies between 16 and 22 mgrms. per 100 c.c. and the sodium content, both in children and adults, between 280 and 310 mgrms. per 100 c.c.

T. J. W.

Estimation of Saccharin in Urine. G. S. Jamieson. (*J. Biol. Chem.*, 1920, 41, 3-8.)—Urine is treated with a solution of normal lead acetate and filtered. The filtrate acidified with hydrochloric acid is extracted with ether, the ether evaporated and the saccharin again extracted from the residue with ether. The ether is removed, the residue fused with sodium carbonate and the sulphur determined as barium sulphate ($\text{BaSO}_4 \times 0.7844 =$ saccharin). Ether is the best solvent (ANALYST, 1914, 39, 354) for the extraction, and good results are obtainable for amounts of saccharin varying from 1 mgrm. and upwards per 100 c.c. of urine. Measured quantities of a standard saccharin solution were added to urines, and the mixtures analysed with very accurate results, the average error when working with from 0.001 to 0.01 gm. of saccharin in 100 c.c. of urine being about 0.0001 gm. A blank determination usually yields about 0.7 mgrm. of BaSO_4 , which should be deducted from that found; the blank should, if possible, be performed on the urine of the subject to be experimented with. Working on 100 c.c. of urine, it was found that about 10 c.c. of a 20 per cent. normal lead acetate solution was a suitable amount to use; excess must be avoided, since precipitation of lead chloride on acidification interferes with the ether extraction; while too little lead acetate leaves matters

present which form emulsions with ether. It is essential to heat urines which contain albumen, almost to boiling for a few minutes before the addition of lead; the subsequent filtration is best effected by suction through a mat of paper pulp about 0.5 cm. thick; this generally occupies about one hour. The filtrate is acidified with 15 c.c. of concentrated hydrochloric acid, followed by 55 c.c. of ether. Elaborate details for the extraction with ether are given in the paper; about 2 grms. of sodium carbonate are used for the fusion in a nickel crucible of the residue finally obtained.

H. F. E. H.

ORGANIC ANALYSIS.

Estimation of Acetaldehyde in Paraldehyde. F. V. Bruckhausen. (*Apoth. Zeit.*, 1919, **34**, 428; *Chem. Zeit. Uebersicht*, 1920, **44**, 77.)—Romijn's method of estimating formaldehyde iodimetrically cannot be adapted to the estimation of acetaldehyde, since the latter reacts with iodine in alkaline solution to form not only iodoform and acetic acid, but also other compounds, so that varying amounts of iodine are consumed. Richter's method, however (*ANALYST*, 1912, **37**, 265), gives trustworthy results, especially when the acetaldehyde and sulphite solutions are cooled to 5° C. before the titration. Paraldehyde containing acetaldehyde consumes permanganate, since it contains hydrogen peroxide. There appears to be a proportional relationship between the amounts of acetaldehyde and hydrogen peroxide.

C. A. M.

Estimation of Dextrose in the Presence of Lactose. E. Hildt. (*Ann. Chim. anal. appl.*, 1920, **2**, 78-80.)—Lactose may be quantitatively hydrolysed by means of sulpho-aromatic acids, as used by Twitchell in the technical hydrolysis of fats. A suitable reagent consists of a solution of 180 grms. of benzene sulphonate (free from iron) in a litre of water containing 49 grms. of pure sulphuric acid. For the hydrolysis of 0.5 to 1 per cent. solution of lactose 20 c.c. of this solution are added, and the liquid heated for six hours in an oven at 95° to 98° C. In applying the method to urine 100 c.c. of the sample are first treated with 10 c.c. of neutral lead acetate solution, and a preliminary test made of the approximate amount of sugar. A volume of the liquid containing not more than about 1 gm. of sugar is mixed with 20 c.c. of the hydrolyzing solution, and made up to 100 c.c., and 50 c.c. of the mixture are heated for six hours at 95° to 98° C. The remainder of the liquid is used for the direct titration of sugars by means of Fehling's solution diluted with 4 volumes of water and treated with 5 or 6 drops of sodium hydroxide solution. The hydrolysed liquid is cooled, made up to 50 c.c. and titrated in the same way, and the results expressed in terms of dextrose or anhydrous lactose, 0.051 gm. of which is equivalent to 0.071 gm. of hydrated lactose, or 0.048 gm. of anhydrous dextrose. From these data the amount of hydrated lactose, x , and anhydrous dextrose, y , in 100 c.c. of the urine may be calculated by means of the equations—

$$x = \frac{3.55}{n'} - \frac{3.55}{n}; \quad y = \frac{1.458}{n'} + \frac{3.34}{n},$$

where n and n' represent the numbers of c.c. of the liquid required to decolorise

10 c.c. of Fehling's solution before and after inversion. In each case these quantities of solution contain an amount of sugars equivalent to 0.051 grm. of inverted lactose.

C. A. M.

Influence of Ester Transposition in the Determination of Saponification Values. A. M. Pardee and E. E. Reid. (*J. Ind. and Eng. Chem.*, 1920, 12, 129-133.)—In the estimation of the saponification value of essential oils it is usual to heat the solution under a reflux condenser, consisting merely of a thin walled glass tube about 1 metre long. The results, however, are frequently low and variable, and in the saponification of acetylated oils, for the estimation of the alcohols present, the error is very much greater. This is due to transposition of the alkyl radical of the ester with the alcoholic medium of the saponifying agent, which takes place at a faster rate than the saponification. The result is that a highly volatile ester is produced in the preliminary stages and methyl acetate or ethyl acetate escapes through the tube of the reflux condenser. For instance, in the saponification of benzyl acetate, an ester boiling at 206° C., the first stage consists in the formation of ethyl acetate, b.p. 77° C., or of methyl acetate, b.p. 54° C., if methyl alcoholic potassium hydroxide is used, and considerable losses may occur. In the saponification of benzyl formate the corresponding formates are produced having still lower boiling points. On the other hand, the saponification of methyl benzoate in methyl or ethyl alcoholic solution will not give rise to highly volatile intermediate products. The authors have investigated this reaction and have shown how unreliable are the results obtained in certain cases when using methyl or ethyl alcoholic solutions. Normal butyl alcohol appears to be the most satisfactory medium in which to carry out the saponification of the esters in essential oils.

J. F. B.

Estimation of Halogen in Organic Substances. W. A. Van Winkle and G. McP. Smith. (*J. Amer. Chem. Soc.*, 1920, 42, 333-347.)—The substance, volatilised with air, is drawn through a heated quartz tube, and the combustion products are absorbed in alkaline sodium sulphite solution; the excess of sulphite is then oxidised with permanganate, and the halogen estimated by Volhard's method. The quartz combustion-tube is about 24 inches long and is slightly inclined, the lower end being bent downwards and connected with the absorption apparatus; the other end of the tube is connected with the volatilisation tube. This consists of a deep test-tube with a side tube near the top and another lower down, the latter reaching well into the end of the combustion tube. The test-tube is closed with a rubber stopper carrying a glass rod for breaking the capsule containing the liquid under examination; a pad of glass wool protects the rubber stopper from attack by the substance. The combustion tube is heated by four wing-top Bunsen burners, an inverted V-shaped asbestos reflector being placed above the tube. The absorption apparatus consists of a vertical tube partially filled with clean sand; the lower end of the tube passes through a cork into a flask connected with a suction pump, whilst the upper end is closed with a rubber stopper through which pass the end of the combustion tube and a short tube connected with a tapped funnel containing the alkaline sodium sulphite solution. During the combustion, a current of air is drawn

through the apparatus and the sodium sulphite is admitted slowly, the top of the absorption tube being so arranged that the solution first flows on to the end of the combustion tube and drips from the latter on to the sand, passing through this into the flask. A secondary current of air is admitted directly into the combustion tube through a side tube. For the analysis of non-volatile substances the volatilisation part of the apparatus and the combustion tube are made in one piece, so that the substance may be heated and burnt in the volatilisation tube and the gases then passed into the combustion tube. The apparatus yields trustworthy results with such substances as ethyl iodide, butyl bromide, benzal chloride, chloroform, *m*-iodobenzoic acid, *p*-bromaniline, etc.

W. P. S.

Study of the Nephelometric Values of Cholesterol and the Higher Fatty Acids.—II. F. A. Csonka. (*J. Biol. Chem.*, 1920, **41**, 243-249.)—A continuation of work previously described by the author (*J. Biol. Chem.*, 1918, **34**, 577). Oleic acid and cholesterol were selected for the investigation because these show the largest difference in their nephelometric values. *Technique A*: Turbidity was produced by the addition of hydrochloric acid after water had been added to the alcoholic solution of the fat. *Technique B*: The alcoholic solution of the fat was added to water and then hydrochloric acid added as above. In Series I. oleic acid and cholesterol were used unmodified, but in Series II. the above substances were saponified by adding 2 c.c. of $\frac{N}{1}$ sodium hydroxide and placing in a boiling water-bath for fifteen minutes. The residue was warmed with 4 c.c. of 95 per cent. alcohol to dissolve the fatty material, and the final volume made up to 50 c.c. with an acidity of $\frac{N}{5}$ hydrochloric acid. For further details the previous paper should be consulted. The nephelometric value varies with the substance employed, the technique adopted, the presence or absence of a protective colloid, and, in some cases, with the period of time elapsing before taking the reading. Tables and curves are given showing the effects of these variables.

T. J. W.

Method of Preparing Phloroglucinol Reagent for the Kreis Test. H. W. Dixon. (*J. Ind. and Eng. Chem.*, 1920, **12**, 174.)—The Kreis test has been found to be useful for the detection and estimation of rancidity in fats, and the phloroglucinol reagent may be prepared in the following manner: 100 grms. of sodium hydroxide are dissolved by heating slowly in a metal vessel with 40 c.c. of water. The melt is cooled to such a temperature that a few crystals of resorcinol dropped into the liquid do not become brown, 15 grms. of resorcinol are then stirred in. The basin is covered with a watch-glass to exclude air, and heated for two to three hours on a sand-bath, taking care not to char the product, until the melt is a dark chocolate-brown. If the reaction is not carried to completion, unchanged resorcinol will interfere with the colour of the Kreis test. The melt is cooled with exclusion of air, then dissolved in about 500 c.c. of water with gentle heat if necessary. The solution is transferred to a beaker, cooled in ice and acidified by the cautious addition of concentrated hydrochloric acid. The acid liquid is extracted repeatedly by shaking with 100 c.c. portions of ether in a separating funnel. The ether extracts are combined and decolorised by shaking with animal charcoal. The filtered ether

extract should be kept as a stock solution. To prepare the Kreis reagent a portion of the stock solution should be diluted with ether until it gives a good reaction with a strongly rancid fat, but a less intense reaction on further dilution. Fifteen grms. of resorcinol should yield 10 litres or more of Kreis reagent.

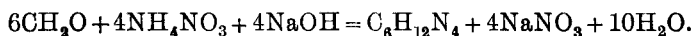
J. F. B.

Change of Refractive Indices of Fixed Oils with Temperature. A. F. Joseph. (*J. Soc. Chem. Ind.*, 1920, 39, 66T.)—In a paper by C. H. Wright (ANALYST, 1920, 52) a formula was given for calculating the refractive index of an oil at the standard temperature of 40° C. from observations made at any other temperature. The author points out that the new formula for temperature correction was hardly necessary, since it shows no advantage in accuracy or simplicity as compared with Tolman and Munson's figures (*J. Amer. Chem. Soc.*, 1902, 24, 754), which showed that dn/dt for different oils is very nearly a constant of value 0.000365. The correction of refractive index for temperature should therefore be made by the simple method of adding or subtracting 0.00036 for every degree of temperature correction.

J. F. B.

INORGANIC ANALYSIS.

Formaldehyde Method for Determining Ammonium Nitrate. J. T. Grissom. (*J. Ind. and Eng. Chem.*, 1920, 12, 172-173.)—With the object of standardising a rapid method for the control of the manufacture of ammonium nitrate the author has investigated the reaction by which hexamethylene-tetramine is produced with formaldehyde, resulting in a corresponding neutralisation of sodium hydroxide. The equation representing the reaction is:



A 20 per cent. solution of formaldehyde neutralised to phenolphthaleïn is added to the ammonium nitrate solution, the mixture is warmed to 60° C., and titrated with $\frac{N}{3}$ sodium hydroxide, using phenolphthaleïn as indicator. This is better than employing an excess of standard sodium hydroxide and titrating back with acid, in which case the results are unreliable, owing to the formation of formic acid. The direct titration method, using $\frac{N}{3}$ sodium hydroxide, gives consistent results which are always about 0.25 per cent. low. This method is recommended for rapid control work, and may be made quite accurate by the addition of a constant correction factor to the results. The factor is determined by performing a Kjeldahl estimation on a representative sample and comparing the result with that obtained by the formaldehyde method.

J. F. B.

Qualitative Analysis in the Presence of Phosphoric Acid. H. Remy. (*Zeitsch. anal. Chem.*, 1919, 58, 385-392.)—The procedure depends on the use of phosphoric acid itself as a group reagent; from an ammoniacal solution, iron, manganese, chromium, alkali-earths, and magnesium are precipitated as phosphates or double phosphates, whilst zinc, nickel, and cobalt form soluble complexes. After heavy metals have been removed by hydrogen sulphide the solution is boiled

to expel excess of hydrogen sulphide, filtered if necessary, and oxidised with nitric acid; the solution is then nearly neutralised with solid ammonium carbonate and poured, with stirring, into an equal volume of warm concentrated ammonia. The mixture is now treated with an excess of ammonium phosphate solution. The phosphate precipitate is collected, dissolved in a small quantity of warm dilute hydrochloric acid, and potassium sulphate solution is added. Barium, strontium, and a portion of the calcium are precipitated as sulphates, and may be separated and identified in the usual way after fusion with sodium and potassium carbonates. The filtrate from the alkali-earth sulphates is boiled with the addition of sodium acetate and ammonium chloride; iron, chromium, and aluminium are precipitated as phosphates, and manganese as ammonium manganese phosphate. The precipitate is collected on a filter, and ammonium oxalate is added to the filtrate (this is still an acetic acid solution); calcium is precipitated as oxalate, whilst magnesium may be precipitated by adding ammonia to the filtrate from the calcium oxalate precipitate. The phosphate precipitate containing iron and other metals is dissolved in hydrochloric acid, the solution heated and nearly neutralised with solid sodium carbonate, and then poured into a mixture of 20 per cent. sodium hydroxide solution and hydrogen peroxide; ferric hydroxide and hydrated manganese dioxide are precipitated, whilst chromium and aluminium remain in solution as chromate and aluminate respectively. After filtration, the iron and manganese may be identified by the usual reactions; aluminium is precipitated on boiling the filtrate with the addition of ammonium chloride, and chromium, already indicated by the yellow colour of the solution, is identified by the perchromic acid reaction. The filtrate from the first phosphate precipitate, and containing the zinc, nickel, cobalt, and alkalis, is heated and treated with ammonium sulphide, and the precipitated zinc, nickel, and cobalt sulphides are collected; zinc sulphide dissolves in dilute hydrochloric acid, whilst nickel and cobalt sulphides remain insoluble and may be identified in the usual way. In the filtrate from the sulphide precipitate, potassium may be identified by the perchloric acid test, and sodium by means of potassium pyroantimoniate. In the case of a mixture free from heavy metals, but containing chromates and permanganates, the preliminary treatment with hydrogen sulphide may be omitted; the chromium and manganese are then found in the solution containing the zinc, nickel, and cobalt phosphates. On treatment with ammonium sulphide they are precipitated as hydroxides and are dissolved, together with the zinc sulphide, by dilute hydrochloric acid. Zinc remains dissolved when this solution is heated with an excess of sodium hydroxide.

W. P. S.

Estimation of Carbon Dioxide, Oxygen, and Combustible Gases by Krogh's Method of Micro-Analysis. H. O. Schmit-Jensen. (*Biochem. J.*, 1920, **14**, 4-24.)—Krogh has described a method of micro-analysis for volumes between 1 and 20 c. mm. (*Scand. Arch. Physiol.*, 1908, **20**, 278; *Abderhalden's Biochem. Arbeitsmeth.*, 1915, **8**, 495).—The principle of the method is based on the fact that small air-bubbles placed in a fluid behave much as semi-fluid fat drops, and easily allow transport from one place to another without disunion. For analysis an air-bubble is sucked up into a capillary tube of uniform bore and measured. The tubes

used by Krogh had a diameter of about 0.25 mm. Gas absorptions are performed one after another in a funnel at the lower end of the capillary tube. Each absorption being finished, the air-bubble is sucked into the capillary tube again and measured anew. Krogh applied this method to the estimation of carbon dioxide, oxygen, and, according to the present author (who acknowledges help from Krogh throughout his research), to carbon monoxide, although there is no mention of this in the papers cited above.

The author found it necessary to devise means for the analysis of gas originating from intestinal gas cysts and containing hydrogen and methane. It was found that Krogh's apparatus served for the estimation of carbon monoxide and hydrogen, using acid cuprous chloride solution, and Paal and Hartmann's solution of colloidal palladium and sodium picrate (*ANALYST*, 1910, **35**, 139) respectively as absorbents. For the estimation of methane it was necessary to devise micro-combustion apparatus. For this purpose the diameter of the capillary was increased so as to admit of the introduction of platinum wires. The diameter finally adopted was about 1 mm. Platinum wires could be introduced into tubes of smaller bore, but the insertion of them into bubbles of 5 c. mm. in tubes of the diameter used by Krogh was made impossible by the surface tension, the bubble escaping when meeting the wire. The apparatus finally adopted is fully described and illustrated in the text, as is a micro-receiver for small gas samples. Carbon dioxide is absorbed in the usual manner, oxygen by alkaline pyrogallol, carbon monoxide by acid cuprous chloride solution, hydrogen is burned with excess of oxygen below a visible heat and methane at a bright red heat. The quantity of gas taken for an estimation is about 80 c. mm., the accidental error of a single estimation ± 0.1 c. mm., and the systematic error in the case of oxygen, hydrogen, methane, and probably carbon monoxide negligibly small. The systematic error in estimations of carbon dioxide, which diffuses with enormous rapidity in most fluids, is relatively large, over +0.5 per cent. in the author's hands. For any one systematic operator, however, and any small range of concentration of carbon dioxide, it should be substantially a constant. G. C. J.

Effect of Chlorides on the Nitrometer Determination of Nitrates. M. T. Sanders. (*J. Ind. and Eng. Chem.*, 1920, **12**, 169-170.)—Determinations were made to ascertain the maximum quantity of sodium chloride which may be present in crude sodium nitrate without introducing a serious error in the estimation of the nitrogen content by means of the nitrometer. Mixtures of known quantities of sodium nitrate and sodium chloride were analysed in the nitrometer with all due precautions, and a curve was plotted showing the percentage error with increase in the proportion of chloride. It was found that the error was reasonably small until the proportions of the mixture rose to 3 mols. of chloride and 1 mol. of nitrate. At this point the curve makes a sharp break upwards, and the presence of more than 3 mols. of chloride to 1 of nitrate makes the estimation quite impossible. It is probable that nitrosyl chloride is formed, which attacks the mercury and liberates nitric oxide which, recombining with free chlorine, repeats the cycle until all the free chlorine is used up. In such a case hydrochloric acid exists in the gases in the measuring tube, and the result is too high. Hence it is concluded that if the percentage of sodium chloride present in the

dry crude nitrate exceeds 15–17, it is impossible to obtain results with the nitrometer which are accurate to 0.1 per cent.

J. F. B.

Preparation of a Hydrochloric Acid Solution of Cuprous Chloride for Use in Gas Analysis. F. C. Krauskopf and L. H. Purdy. (*J. Ind. and Eng. Chem.*, 1920, 12, 158-161.)—A solution of cuprous chloride in excess of hydrochloric acid is recommended by Winkler for the absorption of carbon monoxide in gas analysis. Such a solution may be conveniently and rapidly prepared by dissolving cupric chloride in concentrated hydrochloric acid and reducing the cupric salt by the addition of stannous chloride. By using a slight excess of stannous chloride the cuprous salt is protected against oxidation during transference from one container to another. The presence of stannic and stannous chlorides in relatively large amounts in a hydrochloric acid solution of cuprous chloride does not impair its efficiency for the absorption of carbon monoxide. When the cuprous chloride solution has become saturated with carbon monoxide it may be restored by heating at 60°–70° C. for some hours. The whole of the carbon monoxide is thereby expelled and the regenerated solution is quite as efficient for the absorption of further quantities of carbon monoxide as the original. If a small amount of the copper has become oxidised during the treatment the solution may be decolorised by the addition of a few drops of concentrated stannous chloride solution.

J. F. B.

Estimation of Nitrogen in Nitrocellulose and Inorganic Nitrates by the Nitrometer. E. G. Beckett. (*J. Chem. Soc.*, 1920, 117, 220-235.)—It is shown that the nitrometer method of estimating nitrogen in nitrocellulose invariably yields low results. The interval of time which is allowed to elapse between the introduction of the nitrate and sulphuric acid into the nitrometer and the shaking has a great influence on the results in the case of nitrocellulose; with inorganic nitrates the effect is less. The most trustworthy results are obtained by using 15 c.c. of 92.5 to 94.0 per cent. sulphuric acid, and allowing fifteen minutes to elapse between the introduction of the nitrocellulose and the shaking. In this case the error amounts to about 0.7 per cent. of the nitrogen present.

W. P. S.

Modification of the Thompson Method for the Estimation of Acetic Acid in White Lead. L. McMaster and A. E. Goldstein. (*J. Ind. and Eng. Chem.*, 1920, 12, 170-171.)—The Thompson method is the most reliable one for the estimation of acetic acid in white lead, both for those samples which have not been ground in oil and for those from which the oil has been extracted. The principal drawback in the latter case is due to the difficulty of complete extraction and the distillation of fatty acids which give a turbid distillate and interfere with the titration of the acetic acid. This difficulty is entirely overcome by performing the distillation under reduced pressure. The procedure is as follows: 18 grms. of extracted white lead are placed in an ordinary 500 c.c. flask with 40 c.c. of syrupy phosphoric acid (85 per cent.) and 50 c.c. of water. The flask is heated directly and the material distilled down to a small bulk. Steam is then passed into the flask and distillation continued until about 600 c.c. of distillate are obtained. After adding

about 0.5 c.c. of phosphoric acid the distillate is transferred to a heavy-walled flask fitted with a two-hole stopper. Through one hole passes a tube with a very small capillary bore, through which a minute stream of air may be drawn in during the distillation. Through the other hole is passed a connecting bulb tube attached to a condenser. Distillation is conducted under reduced pressure, corresponding to about 150 mm. of mercury, using a conical filtering flask as a receiver. Distillation is stopped when 10 c.c. of the distillate required only one drop of $\frac{N}{10}$ alkali to produce a colour change in phenolphthalein. At no time should the volume of liquid in the distillation flask be allowed to fall much below 100 c.c., as phosphoric acid may then be drawn over. In this method the final distillate is always obtained clear, and the results are accordingly slightly lower than by the Thompson method, which always yields cloudy distillates. It is possible even to proceed to the analysis without previously extracting the oil.

J. F. B.

Determination of Oxygen by the Copper-Ammonia-Ammonium Chloride Reagent. W. L. Badger. (*J. Ind. and Eng. Chem.*, 1920, 12, 161-164.)—Hempel has described a reagent for the absorption of oxygen in gas analysis, consisting of spirals of metallic copper immersed in a liquid consisting of equal parts of saturated ammonium carbonate solution and ammonia of sp. gr. 0.93. The author has investigated this reagent, but found that it is not the most effective solution of its type for the quantitative absorption of oxygen. The most suitable reagent is made by saturating with ammonium chloride a mixture of one part of concentrated ammonia and one part of water. Such a solution when employed in the absorption pipette in the presence of copper spirals will absorb fifty to sixty times its volume of oxygen. It must then be changed, not because it fails to absorb the oxygen quantitatively, but because such a heavy precipitate is formed that the reagent becomes unmanageable. The solution, however, is still useful for a considerable time after the precipitate begins to form. In the analysis of commercial oxygen, where the residue of unabsorbed gas is very small, care must be taken that one or two of the copper wires project clear up into the entrance to the capillary; for, if the gas residue is not in contact with metallic copper, the last traces of oxygen will not be absorbed. It would appear therefore that the absorption of oxygen depends directly on the oxidation of the metallic copper, and that the function of the solution is merely to keep the metal surface clean and active. This reagent is cleaner to use and lasts longer than alkaline pyrogallate, and it is active at almost any temperature. When fresh, it leaves appreciable amounts of ammonia in the gas, for which reason the burette water should be kept slightly acid. The reagent cannot be used for the estimation of oxygen when carbon monoxide or acetylene is present in the mixture.

J. F. B.

The "Heat-Rise" Method of Testing Sulphuric Acid and Oleum. R. Curtis and F. D. Miles. (*J. Soc. Chem. Ind.*, 1920, 39, 64-65r.)—The "heat-rise," accurately standardised by the titration method, may serve as a simple and rapid test for use in plant control. For this purpose a fairly large sample, 400 grms. of acid, may be taken for the estimation, and the apparatus required consists simply

of an earthenware mug holding about a pint, two measuring cylinders, and a thermometer with a scale marked inside the stem. The standardisation is carried out with samples of oleum and sulphuric acid, the composition of which has been determined with the highest accuracy by the titration method. The results are plotted as graphs, from which the results of subsequent estimations are read off. In all cases the samples should be cooled to at least 25°C . Three types of test are described—(a) *Test for Oleum* (of not more than 25 per cent.): 200 c.c. of oleum at temperature $a^{\circ}\text{C}$. are poured quickly and with vigorous stirring into 200 c.c. of sulphuric acid at temperature $b^{\circ}\text{C}$. in the mug. The maximum temperature, $c^{\circ}\text{C}$., of the mixture is noted, and the rise is $c - \frac{1}{2}(a + b)$. The sulphuric acid should have a strength of between 92.5 and 94.5 per cent. The results are reliable within 0.5 per cent. of free trioxide or 0.1 per cent. H_2SO_4 . After mixing, the liquid should not fume. (b) *Test for Sulphuric Acid* (96 to 100 per cent.): The procedure is as above, but the sulphuric acid is poured into the oleum (20 to 25 per cent. SO_3). After mixing, the liquid should fume. If it does not fume, test again as for a weaker acid (below). Variation in the strength of the oleum, between 18 and 25 per cent., is without effect. The results are reliable within 0.3 per cent. H_2SO_4 . (c) *Test for Sulphuric Acid* (88 to 96 per cent.): 100 c.c. of the acid sample at temperature $b^{\circ}\text{C}$. are mixed with 300 c.c. of oleum (20 to 25 per cent.) at temperature $a^{\circ}\text{C}$. Rise = $c - (3a + b)/4$. After mixing, the liquid should fume. The error should be less than 0.5 per cent. H_2SO_4 . In factory work, where frequent tests are required, the method is extremely useful. The presence of large quantities of impurity affects the results, and it has been observed that oleum made from sulphuric acid recovered from T.N.T. waste acid gave an abnormally high rise of temperature. J. F. B.

Rapid Method for the Determination of Sulphur in Petroleum Oils.

A. W. Christie and C. S. Bisson. (*J. Ind. and Eng. Chem.*, 1920, **12**, 171-172.)—After the combustion of 0.5 to 0.6 gm. of the sample in a calorimetric bomb with oxygen under a pressure of 30 atmospheres for the determination of the calorific value, the whole of the sulphur present in the oil has been oxidised to sulphuric acid. The contents of the bomb are washed through filter-paper into a 250 c.c. beaker, and the total acidity of the liquid is determined by titration. The solution is then made up to a definite volume such that an aliquot portion of 25 c.c. will contain between 0.2 and 1.5 mgrm. of sulphur. A portion of 25 c.c. is measured out into a 300 c.c. wide-mouthed conical flask and acidified with one drop of dilute hydrochloric acid; 10 c.c. of a solution of benzidine hydrochloride (8 grms. per litre) are added, the solution is shaken several times and allowed to stand for fifteen minutes or longer. The benzidine sulphate is collected in a Gooch crucible on an asbestos pad which has previously been treated with permanganate. The flask is rinsed three times with 5 c.c. of cold water, each portion being drained through the filter before the next is poured on. The asbestos pad and precipitate are then washed back into the original flask. One c.c. of 10 per cent. sodium hydroxide is added and the flask is warmed on the steam-bath to dissolve the benzidine sulphate. Water is then added to bring the volume up to about 100 c.c. and 5 c.c. of concentrated sulphuric acid are added. The flask is placed on the steam-bath and the solution is

titrated hot with $\frac{N}{20}$ permanganate until the red colour fades slowly. An excess of 10 c.c. of permanganate is added, and heating on the steam-bath continued for exactly ten minutes. Ten c.c. of $\frac{N}{20}$ oxalic acid are added, and as soon as the solution clears the titration is finished off with permanganate. The net consumption of permanganate is multiplied by the factor 0.041 to obtain the number of mgrms. of sulphur in the portion of original solution taken, this factor having been ascertained by the analysis of known solutions of sulphates. The results are essentially the same as those obtained by the gravimetric barium sulphate method. By using the entire rinsings of the bomb and concentrating to 25 c.c., accurate results may be obtained for oils containing only 0.1 per cent. of sulphur. J. F. B.

Estimation of Tin. J. M. Kolthoff and R. Van der Heyde. (*Pharm. Weekblad*, 1919, 56, 1466; *Chem. Zeit. Übersicht*, 1920, 44, 65.)—The tin solution, the acidity (hydrochloric) of which should be about 4*N*, is treated with two drops of 1 per cent. antimony solution and 0.2 gm. of reduced iron, and boiled until the iron is dissolved, the mouth of the flask being meanwhile covered with a funnel. After the reduction a fragment of marble is added, so that the carbon dioxide produced will protect the stannous chloride from atmospheric oxidation, and the liquid is rapidly cooled. It is then diluted with 100 c.c. of water, free from air (prepared by adding 1 gm. of sodium hydrogen carbonate and a little hydrochloric acid to 100 c.c. of distilled water), an excess of $\frac{N}{10}$ iodine solution immediately added, and the excess titrated with sodium thiosulphate solution. The method is also applicable in the presence of considerable amounts of antimony as found in alloys. In such cases the mixture of tin and antimony is dissolved in strong sulphuric acid, the solution boiled with reduced iron and hydrochloric acid and filtered after reduction, and the filtrate treated as described. C. A. M.

Approximate Quantitative Microscopy of Pulverised Ores. W. H. Coghill and J. P. Bonardi. (*Techn. Paper*, No. 211, Bureau of Mines Dept. of Interior, U.S.A., 1919, 20 pp.)—Hynes' method of sorting pulverised minerals by the use of a reading-glass and microscope (*Min. and Sci. Press*, 1915, 110, 994) has been simplified and developed. The best apparatus for the purpose is a binocular microscope with a stage adapted for rapid orientation. The pulverised ore for each reading is oriented by adjusting it along a ruled off-set, each square of which has a distinguishing letter. Although only a part of the grains sprinkled on to the slide is counted, groups of them are taken systematically as in ordinary sampling. The most satisfactory illumination is obtained when dark-green paper is placed as a background beneath the glass slide. Close grading by means of screens is essential, and the separated products should be washed and dried so as to show clear-cut surfaces. Coarser products should be sprinkled on to the slide, so that each field contains about a dozen grains, whilst finer products should be sifted on to the slide. In preparing samples it is best to begin with wet screening on the finest sieve, and for this purpose a solution of saponin or of soap is much more satisfactory than water. In calculating the weight of constituents from the volumes counted, chemical analysis and familiarity with the ore in question will afford guidance. For example,

in the case of molybdenite concentrate the siliceous gangue has a weight factor of 1, whilst pyrites and equivalent molybdenite in "locked" grains have a factor of 2, and free molybdenite flakes (which break into thin flakes about half as thick as the other grains) are assigned a factor of 1, instead of 2, in accordance with their specific gravity. A camera lucida sketch of the outlines of the powdered mineral as seen through a monocular microscope affords a trustworthy criterion of the nature of an ore.

C. A. M.

APPARATUS, ETC.

Analytical Weighing. H. L. Wells. (*J. Amer. Chem. Soc.*, 1920, **42**, 411-419.)—The author recommends the adoption of short swings of the balance in weighing, and adduces many arguments against long swings.

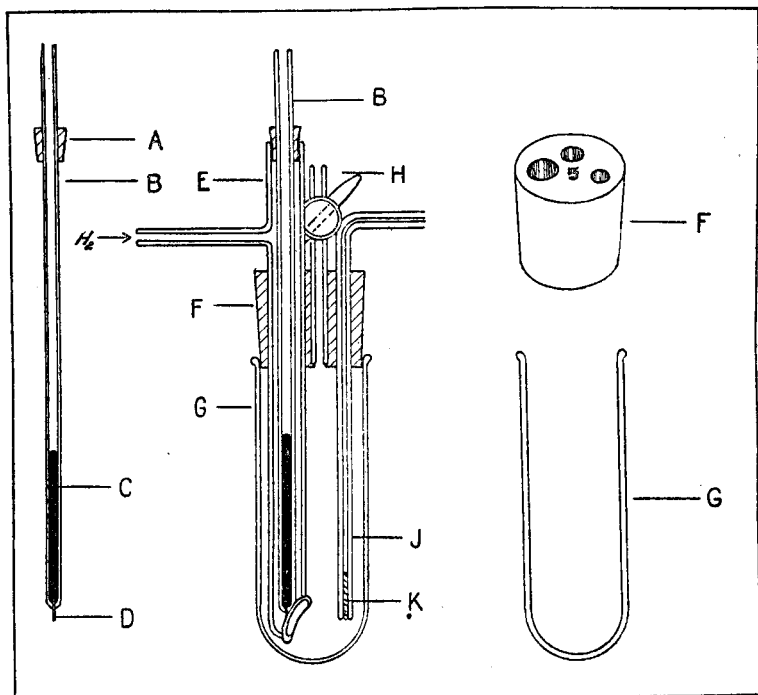
W. P. S.

Modification of the Apparatus for the Estimation of Arginine Nitrogen by Van Slyke's Method. G. E. Holm. (*J. Amer. Chem. Soc.*, 1920, **42**, 611-612.)—A Kjeldahl flask, having a short neck, is closed with a rubber stopper, through which pass a short tube for the introduction of liquids and the stem of an "anti-spray" bulb; this stem is longer than usual, and around it is fitted a short condenser. During the alkali digestion, water is passed through the condenser; the contents of the flask are then allowed to cool, the water is drained from the condenser, 200 c.c. of water and a quantity of zinc dust are added to the flask through the short tube, and the distillation is continued in the ordinary way.

W. P. S.

Determination of Hydrogen Ion Concentration. J. W. M. Bunker. (*J. Biol. Chem.*, 1920, **41**, 11-14.)—An electrode and vessel are described which fulfil the necessary requirements for easy and accurate work on the reactions of culture media and other biological fluids. The apparatus is a modification of the bubbling electrode used in a glass vessel, the essential part of the apparatus being the tube *E* used to conduct the hydrogen gas to the platinum wire of the hydrogen electrode. This is a piece of glass tubing of $\frac{5}{16}$ inch internal bore, with a side arm of small diameter joined to it at approximately 1 inch from the top, the total length being about 5 inches. In its preparation it is sealed at the bottom and then heated on one lower "corner," and a bubble at this point is blown and later broken with a file. The edges of the lip which remain are fire-polished and then the end of the tube is sealed, and the round hole thus obtained is contracted to an approximately oval shape. The hydrogen electrode itself, *B*, is made from a piece of $\frac{1}{8}$ inch tubing and a short piece of platinum wire sealed in at the bottom, projecting outside about $\frac{1}{8}$ inch, and inside far enough to make contact with the mercury *C*, the entire electrode being about 6 inches long. The tube *B* with the stopper *A* is inserted in tube *E* and adjusted so that *D* is opposite the oval orifice. When gas is bubbled through there should form a large bubble at the base of the tube *E* which is held together by the walls of the tube until it has travelled far enough for the level of the liquid within the tube to have reached a point below the platinum wire; it is thus

exposed to hydrogen gas. Electrode vessel *G* is an ordinary test-tube of 1 inch internal diameter and about 3 inches long, and when a series of determinations of P_H is to be made the proper number of tubes is selected, and one by one each may be pushed up under the electrode against the rubber stopper *F*, which has three holes



made in it to receive tightly the tube *E* and the outlet tube *H* with its stopcock, and also to receive, but not too tightly, the potassium chloride arm *J* made of small capillary tubing. Numerous working details are given, for which the original paper must be consulted.

H. F. E. H.

Problems and Fallacies of Sampling. W. L. Baillie. (*Chem. Trade J.*, 1920, 66, 333-336.)—This paper indicates the great importance of accurate sampling and the difficulties met with in its achievement. The experimental error in sampling should be of such an order that it will not increase the experimental error in the method of examination involved. Any degree of refinement is possible by taking increasing numbers of very small portions evenly from different parts of the bulk, but the probable error is inversely proportional only to the square root of the number of portions forming the sample, and this method of increasing accuracy soon becomes impracticable. When sampling materials received in numerous packages where no wilful adulteration is suspected, and the impurities consist of harmless diluents, it is probably sufficient to sample one in five packages in consignments of fifty or over, but a higher proportion is advisable in smaller lots. When, however, the impurities are liable to consist of intentional adulterants or are of an objectionable nature, the only

alternative is to sample from most or all of the packages. The importance of this latter method is illustrated by a table (quoted from Hill) showing the variation in content of arsenic and lead in different casks of a consignment of boric acid :

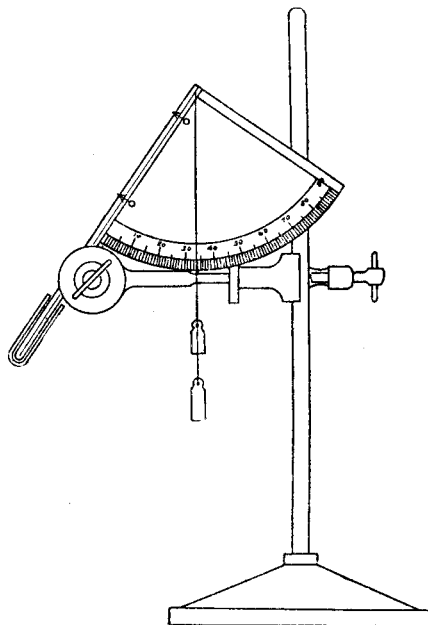
Number of Cask.	Parts per Million.	
	Arsenic.	Lead.
2	10	4
4	15	2
6	2.4	2
8	0.4	45
10	0.4	24

If the contents of any particular package differ in appearance, colour, odour, etc., from the remainder of the bulk, samples should be taken from this and each of the neighbouring units ; also a larger proportion should be taken from the first and last few packages of any delivery, particularly if the material is made by a discontinuous process. In many cases samples from different packages of a consignment may be kept separate for moisture determination, and then mixed and resampled for the remaining determinations. The amount and distribution of impurities is frequently very variable, even in a single parcel, and with some mixed materials (*e.g.*, dynamite) the composition is liable to vary owing to segregation on standing. In such cases extreme care is necessary to ensure a truly average sample. When liquids are sampled, solid foreign matter may generally be mixed uniformly by rolling or stirring, but if this is impossible a special sampling instrument must be employed. In addition to obtaining a representative sample such questions as the suitability of containers, methods of storage, means of transit, etc., must be considered. Any receptacle should be unacted upon, either physically or chemically, by the material of which the sample is composed, and should be closed in such a manner that no constituent of the sample can be lost by evaporation. With regard to labelling, this should be as complete as possible, for neglect of this precaution often leads to much unnecessary trouble and waste of time. Examples of research applied to the sampling of copper bullion and wood pulp are given, and indicate that the question of sampling is by no means a simple matter, and that an efficient sampler must possess skill and knowledge of a high degree. Several devices employed for sampling consignments of materials and for the control of manufacturing operations are described in detail, and tables illustrating various points dealt with in the text are provided.

T. J. W.

Surface Tensimeter for Small Quantities of Liquids. C. C. Kiplinger. (*J. Amer. Chem. Soc.*, 1920, 42, 472-476.)—An apparatus for measuring surface tension which requires only a few drops of the liquid is shown in the figure. A capillary tube, 18 cm. in length and 1 mm. internal diameter, is fixed to the edge of a graduated

quadrant (this may be cut from a celluloid protractor). A short column of the liquid is introduced into the capillary, the lower end of the latter is closed with a glass cap to retard evaporation, and the tube is then turned to such an angle that the meniscus at the lower end of the liquid changes to a plane surface. This angle is given by the weighted threads attached to the apex of the quadrant, two threads being used to eliminate parallax. If A is the angle and L the length of the liquid layer in the capillary (measured to 0.1 mm.), then $L \cos A = h$, where h is the height of the



vertical column exerting the same downward pressure as the inclined layer of liquid. The formula

$$T = \frac{d \times h \times r \times 980}{2} \text{ dynes per sq. cm.}$$

is used in the calculation of T , the surface tension. Results obtained by the use of the apparatus with water, benzene, carbon tetrachloride, toluene, and ethylene dibromide are concordant but uniformly lower by a few units than the correct values; this may be due to a slight change in the length of the liquid layer owing to the flattening of the meniscus, and the need of a correction factor is indicated.

W. P. S.

Thermoregulator with the Characteristics of the Beckmann Thermometer. R. B. Harvey. (*J. Biol. Chem.*, 1920, **41**, 9-10.)—With low temperature regulation it is desirable to reduce the heat capacity of the regulator as much as possible in order to effect quick response, and it is also advisable that the thermoregulator should show the same lag effects as the standard Beckmann thermometer. An instrument is described and illustrated which can easily be set at any temperature

between -20 and $+250^{\circ}\text{C}$. The approximate setting is made by warming or cooling the mercury bulb until the upper level of the column reaches the desired point on the setting scale, while, for more accurate settings, a series of small globules of mercury is detached from either portion; as many of these droplets as are desired can be added to the contents of the bulb by turning the instrument upside down. The setting is easier than with the ordinary Beckmann thermometer, and the lower platinum contact should be made in an enlargement of the capillary to prevent sticking of the mercury at this point, the upper contact being placed at the end of the capillary so that small temperature changes will make or break the circuit. The mercury column is of sufficient diameter to carry the current desired to operate a 150 ohm relay using 2 or 4 volts. The heating circuit should be broken by a relay.

H. F. E. H.

New Turbidimeter for Solutions of Gelatin, Cellulose and Varnishes.

S. E. Sheppard. (*J. Ind. and Eng. Chem.*, 1920, 12, 167-169.)—For the measurement of the clarity of viscous solutions the most convenient method is that depending on the extinction of visible details in some standard object. In the method described, the thickness of liquid under examination and the conditions of illumination are kept constant while the visibility of the object is varied continuously. For this purpose the author employed cross gratings similar to those used by Ives for his test object for visual acuity. The essential part of the apparatus consists of two superposed opaque line gratings arranged to rotate relatively to each other about an axis perpendicular to their plane. Viewed by transmitted light at such a distance that the grating lines are below the limit of resolution, parallel dark bands are seen. When one plate is revolved over the other the separation of these bands alters continuously until a point of invisibility is reached when the bands can no longer be resolved. If the bands are viewed through a turbid solution the point of invisibility is reached with a smaller angle of rotation. The instrument comprises a source of light, consisting of a concentrated filament lamp and hood, a mirror for reading the scale, diffusing and reducing glasses, the crossed gratings with vernier and scale, a cell for holding the samples in the path of light in front of the gratings, a tube, and eyepiece. The samples are preferably placed in square-sided, 8-oz. bottles with screw covers, and, since these are not accurately made, they are immersed in the parallel glass-walled cell containing a medium such as monochloronaphthalene which has the same refractive index as the glass. Readings are first taken with clear water, and the rotation of the gratings necessary to extinguish the resolution of the bands is determined ($\text{angle} = A \text{ max.}$). The jar containing the fluid to be tested is then placed in the cell and the rotation corresponding to extinction again determined ($\text{angle} = A$). A sufficiently accurate comparison is obtained by taking the percentage ratio of A to $A \text{ max.}$ as the clarity value compared with the standard liquid.

J. F. B.



REVIEWS.

ALCOHOL: ITS PRODUCTION, PROPERTIES, CHEMISTRY, AND INDUSTRIAL APPLICATIONS.

By CHARLES SIMMONDS, B.Sc. London: Macmillan and Co. 1919. Price 21s. net.

It does not always fall to the lot of an author to produce a scientific treatise at a time so peculiarly opportune as that selected by Mr. Simmonds. The conviction of the sub-committee on motor fuel that the only ultimate solution of the motor problem is the production of home or empire-produced power alcohol, the re-appointment of Sir Frederick Nathan as Power Alcohol Investigation Officer on the Fuel Research Board, and the necessarily increasing quantity of alcohol which is required for our expanding manufacture of dyes, synthetic drugs, etc., is ample testimony to the national importance of the production of alcohol.

Mr. Simmonds' work is of a standard character, and its compilation shows internal evidence not only of great care and accuracy, but also of scholarly enthusiasm for his subject. The arrangement is admirable, and a judicious balance is maintained of the relative importance of the several matters dealt with. The reviewer is tempted to take his readers for a mental tour through the different chapters, but he must be content with drawing attention to some of the more important aspects of the author's work. A brief introductory chapter of an historical character is followed by one dealing with the production of alcohol. A good account is given of the "Amylo" process of fermentation, and in this connection it is greatly to be deplored that our Customs and Excise regulations prevent advantage being taken of any benefits which the process may offer, or of any developments to which it may give rise. Technical progress is impeded because of the statutory requirement that the distillers' wort before fermentation shall be ascertained by means of the saccharometer, and this, unfortunately, is impracticable in the "Amylo process." A better instance of bureaucratic short-sightedness would be hard to find. The production of alcohol from wood is described, and although the results so far have not been financially successful, yet in the opinion of some technologists there is a future for the Classen process. The fact that several millions of gallons of alcohol have been produced from wood waste lends support to the view that ultimate success is probable. The main difficulties appear to be of an economical character.

The manufacture of methyl alcohol is described, and useful tables are given of densities of mixtures of methyl alcohol and water.

The analytical side, as might be anticipated, has been dealt with by Mr. Simmonds in a most lucid manner, and for this—if for no other—reason the volume will find a place in the book-shelves of those practitioners who are interested in alcoholometry and the analysis of alcohol, acetone, spirits, wines, etc. The position of industrial alcohol, the composition of denatured and specially denatured alcohols, foreign denaturants, and the various official regulations attaching to their use, are discussed. The preparation of ether, chloroform, ethyl chloride, bromide and iodide, chloral ethyl acetate, ethyl acetoacetate, and other technical ethyl and methyl compounds, is described.

The matter dealing with alcohol as a source of motive power and the author's

résumé of the most recent reports and investigations on this subject will be read with interest by those who are concerned with this far-reaching and important problem.

That portion of the book dealing with the chemical examination of potable spirits and the advantages and defects of the Allen-Marquardt, Beckmann, Government Laboratory, and other methods of estimating higher alcohols will be read with professional interest by the analyst. The analysis of beer, cider, perry, and wines is gone into in a fairly comprehensive manner. Included in the first mentioned is the volumetric determination of original gravity, which constitutes a useful brewery control method.

The final chapter, dealing with the physiological effects of alcohol, is based on the valuable review recently compiled by the Central Control Board (Liquor Traffic) of the United Kingdom.

The author is to be heartily congratulated on the production of a volume which is a real contribution to a highly important branch of chemical literature.

EDITOR.

A TREATISE ON QUALITATIVE ANALYSIS. By F. CLOWES and J. B. COLEMAN.
Ninth edition. Pp. 416. London: J. and A. Churchill, 1920. Price 12s. 6d. net.

The new edition of this well-known work on qualitative analysis can be strongly recommended as a book which may safely be put into the hands of all students engaged in the study of this important subject.

In the training of those who attend the laboratories of our schools and colleges, it is most desirable that the qualities of accuracy, carefulness, and attention to detail should be inculcated from the beginning, and the teacher of practical chemistry will find that this text-book provides valuable assistance in the task of instructing those placed in his charge.

This edition is enlarged and revised. The section on the preparation of gases which appeared in former editions has been deleted, and this has allowed space for a fuller treatment of matters relating to analytical practice. A further improvement is the arrangement of the reactions of the metals so that they are now placed in their natural order, and formulæ, such as KHO, have been rewritten KOH etc.

In the first two sections, apparatus and general manipulation are thoroughly treated in a manner calculated to induce in the student a respect for *method* and clean working. A better diagram of the Bunsen flame should be given, showing its various parts, and instructions for cutting glass tubing of wide bore might be included.

In a book which claims to be a *treatise*, a more up-to-date account should be given of the spectroscope and of the various methods of illumination employed in working with it, as well as a description of the means employed for ascertaining the wave-lengths of the spectrum lines. The treatment of the subject is too elementary.

In the section dealing with analytical reactions, the theoretical side of the subject has received far less attention than it merits. Surely, the scientific foundations of analytical chemistry give spirit and life to the subject, and are calculated to stimulate enthusiasm. No mere consideration of *space available* should allow this aspect of the subject to be almost ignored.

The two following sections deal with the reactions of the metals and acid radicles. The explanations are clear and concise, and the treatment thorough. The reactions of the rarer elements are included, together with tables by means of which the various metals and acid radicles may be separated and identified. In this connection it would be a great advantage if, in presenting two or three alternative schemes of separation, the authors would give us the benefit of their experience, and state which scheme is advisable under any given set of conditions.

There is no mention of the following reactions which are now extensively employed, and which should be given in a book of this scope—namely, cupferricⁱⁿ for the precipitation of iron and titanium, the hydrogen peroxide test for titanium, the dimethyl-glyoxime test for nickel, and the α -nitroso- β -naphthol test for cobalt; also the ammonium cobalto-thiocyanate test for this last metal.

Further omissions are: the sulphanilic acid and α -naphthylamine test for nitrites, the perchloric acid test for potassium, the sodium cobalti-nitrite test for that metal, and the pyroantimoniate test for sodium. It is not made sufficiently clear that lithium carbonate is not precipitated in the barium group in the presence of much ammonium chloride, and the formula for ammonium metavanadate is wrongly written.

There is a useful section dealing with the reactions of the more common organic compounds, and on the identification of gases; the portion dealing with the analysis of complex mixtures, minerals and acid radicles is particularly good, and includes ample explanations of numerous important points.

The tables given for the separation of the rarer metals need some extension, in particular, that dealing with the analysis of rare earth minerals.

Sound advice is given concerning laboratory fittings and arrangements, and the expression of the concentration of reagents in terms of normality is rightly advocated.

The book is full of useful information, and the numerous cross-references have permitted the inclusion of much matter within a small compass. It will no doubt find increasing favour among teachers and analysts.

The authors are evidently exponents of the gospel of *orderliness* and the *clean bench*, factors so essential to all good work. The spirit of the book is an antidote against haphazard and "slapdash" work which so easily spoils an otherwise promising student, and the authors are to be congratulated upon providing us with such an excellent treatise on the subject.

A. J. HALE.

ANNUAIRE POUR L'AN, 1920. Paris: Gauthier-Villars et Cie. Price 4 fr. 50 c.

This little book is published under the ægis of the Bureau des Longitudes, and appears to have been issued regularly since 1796.

It contains an immense mass of useful information in the fields of astronomy, meteorology, geography, chemistry, and physics. Among the information likely to be useful to the chemist, one notices the numerous tables giving the densities of pure substances and of minerals, co-efficients of expansion, vapour tensions, specific heats, indices of refraction, specific rotatory powers, and many other chemical and physical data.

There are also brief but clearly written explanatory chapters dealing with such subjects as alcoholometry, radio-activity, calorimetry, etc.

The compilers and the Bureau des Longitudes are to be congratulated on the evidence of careful selection which this little book reveals, and on having compressed such a vast amount of useful matter within so small a compass. As a "pocket-book" of general reference it is one of the best which has come under the writer's notice.

A. CHASTON CHAPMAN.

CATALYSIS IN THEORY AND PRACTICE. By E. K. RIDEAL and H. S. TAYLOR. Pp. 496. London: Macmillan and Co. 1919. Price 17s. net.

The great interest of catalysis to chemists in general rests chiefly on two facts. First, catalytic action is so general that it is questionable whether any reaction has ever been conducted without catalysis, and, second, such explanations as have been advanced are obviously primitive and tentative, and afford little assistance to the chemist who is in search of the most suitable catalyst for some particular reaction. Probably no greater service could be rendered to the science, both theoretical and applied, than the formulation of a satisfactory general theory, or set of theories, to explain catalytic action. If and when this is accomplished, chemical action in general will doubtless be understood in a manner altogether more fundamental than is the case to-day.

If the reader of the volume under review expects to find in it new light on catalytic processes, he will be disappointed. The work is purely a compilation from previous publications, with occasional notes from the authors' own experience and, here and there, remarks on possible directions for future research. The discussion of theory is slight and uncritical. It follows, on the whole, the Ostwald dogma.

Regarded as a compilation, the work has much in its favour. It is comprehensive, as the following titles of its chapters indicate: Early History; Theoretical Introduction; Measurement of Reaction Velocity in Catalytic Processes; Oxidation Processes; Hydrogen and Hydrogenation; Dehydrogenation; Fixation of Nitrogen; Hydration and Hydrolysis; Dehydration; Applications of Catalysis to Organic Chemistry; Ferments and Enzymes; Catalysis in Electrochemistry; Catalysis by Radiant Energy; Catalysis in Analytical Chemistry.

The analytical chemist will probably turn first to the last chapter, of some forty-three pages, as embodying his immediate interests. It is doubtful whether he will find anything of novelty in it, but if he is not in touch with other developments of the science he may obtain hints from other sections of the work which will enable him to choose a suitable catalyst for some reaction which he desires to accelerate. In the present state of the theory there can be only occasionally any certain guide in this matter.

The book is pleasingly printed, but with rather more "printer's errors" than should have escaped correction. The references are numerous, but at times seem to have been overlooked—*e.g.* pp. 179-182. In other ways also there is evidence that the production has been hurried—*e.g.* the reader is supplied with many chemical equations which he could be trusted to know (*e.g.* the one on p. 139), while the less

familiar formulæ of mathematical physics are employed with no, or little, explanation. These minor faults may well be corrected in a second edition.

H. F. COWARD.

THE PROFESSION OF CHEMISTRY. By RICHARD B. PILCHER. Pp. xiv and 199. ¹⁹¹⁹
London: Constable and Co., Ltd. 1919. Price 6s. 6d. net.

The choice of a career for a boy or girl is generally a difficult matter, and especially so when those with whom the choice lies are unacquainted with the means and qualifications necessary to success in the career that may be contemplated. No one perhaps is better qualified than Mr. Pilcher to advise as to training for the chemical profession, and his book bears the impress of thorough knowledge of his subject. The book will prove extremely helpful to parents and guardians who have this profession in view for their charges, as well as to the youthful aspirants themselves. Many who entered the profession years ago have since had occasion to regret that the advice contained in this book was not available when it could have been of use to them.

Mr. Pilcher takes a comprehensive view of his subject, beginning with general education at school, passing thence to college or university training, and finally outlining the special qualifications requisite in the various branches of the profession. Naturally and properly much space is devoted to the requirements of the Institute of Chemistry. The section on "Pharmacists and Chemists" will be especially instructive for those for whom the book is primarily intended; a good case is made out for the claim to the title "Chemist" of those who have studied the science generally, as distinct from those who have studied the one branch of applied chemistry known as pharmacy. The section on "Professional Training" includes a useful list of Institutions where special courses in various branches of applied chemistry may be obtained. In the section on "Professional Procedure" Mr. Pilcher upholds a high standard of conduct, and in dealing with the subject of advertising he quotes very aptly an opinion of Dr. Johnson, who, whilst condemning solicitation for employment by a lawyer, said: "I would have him inject a little hint now and then to prevent his being overlooked." The "little hint" must be allowed to chemists as well as to lawyers, though of course much depends on the manner of application. The book concludes with a short account of the services rendered by chemists during the late war. In reference to the Gas Services it is remarked that "High qualifications were unnecessary for the work of the rank and file," a statement that will be contradicted by none.

Mr. Pilcher does not hold out illusory hopes of riches to those who intend to enter the profession, and indeed the impression left on the mind of the reader is that, whilst the study of chemistry demands high thinking, the practice of it enforces rather plain living. That this impression is correct will be generally admitted. It is unfortunately the case that the man who has spent some of the best years of his life in training to become a chemist often finds his services less well rewarded than those of the man who has passed direct from school to commercial work. It may be that this condition is one of unstable equilibrium, and that time will effect an

improvement. The attitude adopted by Government and Municipal authorities towards the profession and towards science generally is largely responsible for the present unsatisfactory state of affairs. It is to be hoped that the Government will profit by the lesson of the war in this respect and learn wisdom from our late opponents.

L. EYNON.

INTRODUCTION TO PHYSICAL CHEMISTRY. By JAMES WALKER, LL.D., F.R.S.
Eighth Edition. Pp. xiii + 433. London: Macmillan and Co., Ltd. 1920.
Price 16s. net.

The first edition of this excellent book appeared twenty years ago, when the English-reading student of chemistry was almost entirely dependent on translations of German textbooks of physical chemistry. It was at once widely adopted as a textbook in our universities and colleges, and, from the fact that an eighth edition has recently been called for, it is clear that the work is still highly esteemed by teachers and by students.

It is unnecessary to describe in detail the plan of a work so familiar to all students of chemistry as that under review. In the eighth edition the general plan of the first is still found, but the necessary revision has, of course, been carried out for the purpose of bringing the information up to date, and new material also has been introduced. We have then before us a perfectly modern, lucidly written elementary textbook of physical chemistry, in which the student will find the fundamental facts and theories of physical chemistry clearly set out, and their importance in the older branches of the subject indicated.

At the time when the book under review was first published, the author felt the necessity of effecting a connection between the ordinary chemical knowledge which the student was supposed to possess and the new material forming the content of physical chemistry. By the method of treatment adopted by the author it was hoped to prevent the student from shutting up his knowledge of physical chemistry in a water-tight compartment, and so failing to perceive its connection with and importance for the proper understanding of the chemistry of inorganic and organic substances. One would hope that the same necessity does not exist to-day. The older manner of teaching inorganic chemistry has, with the growing up of a new generation of teachers, largely disappeared, and many of the more important facts and theories of physical chemistry are now introduced in the appropriate manner even in the elementary courses in inorganic chemistry. The teaching of organic chemistry, it is to be hoped, will similarly undergo changes under the influence of physical chemistry. Although, therefore, the necessity for emphasising the organic connection between physical chemistry and the older branches of the subject may not be so great as formerly, the work by Professor Walker will be found of the greatest value to the teacher who desires to keep the unity of the subject constantly before the minds of his students.

In the present edition two new chapters make their appearance, dealing with the dimensions of atoms and molecules, and with atomic number. In reading through these chapters dealing with such important matters, the reviewer could not

but feel that the author had carried the process of condensation rather far, and he would venture to suggest that a somewhat fuller treatment might be given to these subjects in a future edition.

To those familiar with Professor Walker's book it is only necessary to say that the present edition preserves the high standard and good qualities of the earlier editions; while to those who have not yet become acquainted with the work, the warmest recommendation can be given.

A. FINDLAY.

MINISTRY OF HEALTH.

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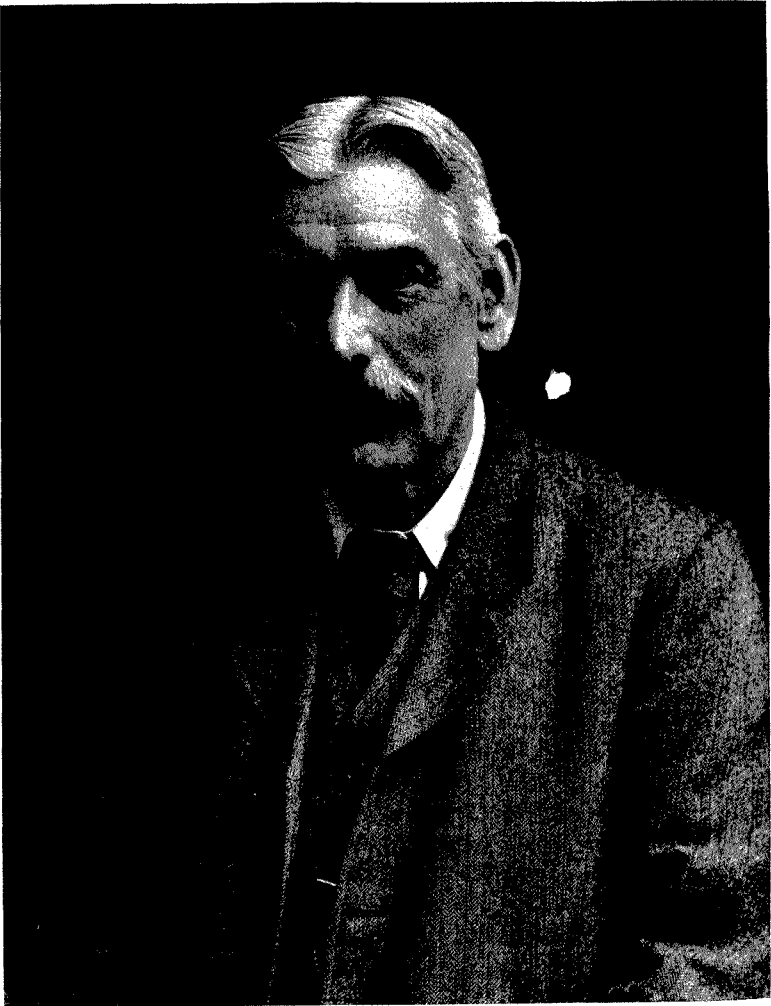
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W. W. Fisher