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The Determination of Organic Peroxides.

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(*Read at the Meeting, May 1st,* 1929.)

THE object of this investigation was to discover a reliable method for the determination of the peroxide-oxygen content of oxidised linseed oil and of certain oxidation products of the glyceride of β-elaeostearic acid (Morrell and Marks, *J. Oil and Colour Chem. Assoc.*, 1927, **10**, 197). Fahrion employed the following method for the estimation of the peroxide-oxygen in oxidised linseed oil:

A sufficient quantity of the material is dissolved in glacial acetic acid, 1 c.c. of 50 per cent. sulphuric acid is added, and 2 c.c. of cold saturated potassium iodide solution. After standing for 1 hour the mixture is diluted with 50 c.c. of water, and the liberated iodine is titrated with $N/10$ sodium thiosulphate solution.

This method was first fully examined with the use of benzoyl peroxide as a criterion. A quantity of 0·2 to 0·3 grm. of the pure material, which had been crushed under dry ether and dried in a current of warm air, was dissolved in 25 c.c. of glacial acetic acid. (Glacial acetic acid is a good solvent both for partially oxidised linseed oil and other peroxides examined.) The reagents were added as set out in Table I, and the mixture allowed to stand in the dark. The product was diluted to about 100 c.c. with distilled water before being titrated, and a blank determination was made in each case.

The calculated peroxide-oxygen content of benzoyl-peroxide, $(C_6H_5COO)_2$, is 6·61 per cent.

TABLE I.

Estimation of peroxide-oxygen content of benzoyl peroxide in *glacial acetic acid* solution under various conditions.

Expt. No.	Amount of sulphuric acid (and water) added.	Amount of potassium iodide added.	Period of standing.	Temp.	Peroxide-oxygen found. Per Cent.
1	none	2 c.c. of saturated cold solution	10 minutes	Room	6·6
2	½ c.c. 98 per cent.	,,	,,	,,	6·6
3	1 ,, ,,	,,	,,	,,	6·4
4	2 ,, ,,	,,	,,	,,	4·4
5	1 ,, 50 per cent.	,,	,,	,,	6·7
6	1 ,, ,,	,,	24 hours	,,	6·6
7*a*	1 ,, ,,	,,	48 ,,	,,	7·3
7*b*	1 ,, ,,	,,	,, ,,	,,	7·2
8	1 c.c. 50 per cent. + 5 ,, water	,,	10 minutes	,,	7·1
9	1 c.c. 50 per cent. + 7 ,, water	,,	,, ,,	5°–10° C.	6·2
10	1 c.c. 50 per cent. + 11 ,, water	,,	24 hours	5°–10° C.	4·1
11	none	2 grms. solid	48 ,,	,,	7·3
12	,,	,,	1 ,,	50° C.	6·7

The following conclusions can be drawn from the above series of experiments.

(1) A theoretical result is obtained thus (Expt. No. 1): Dissolve 0·2 grm. of the peroxide in 25 c.c. of glacial acetic acid; add 2 c.c. of concentrated cold potassium iodide solution (or 2 grms. of the powdered solid); mix and allow the mixture to stand for a few minutes; dilute with about 100 c.c. of distilled water, and titrate with *N*/10 sodium thiosulphate solution. A blank test must be made, and its result deducted. Ordinary potassium iodide (not necessarily free from iodate) and ordinary pure sulphuric acid were employed in the above experiments, but it is recommended to use both these reagents of "A.R." purity.

(2) The quantity of sulphuric acid added, if any, should not exceed 0·5 c.c., and either concentrated or 50 per cent. acid can be employed (compare Experiments 1 to 5). The potassium liberated from the potassium iodide forms potassium benzoate in the absence of sulphuric acid (see equation below); hence addition of sulphuric acid is unnecessary (Expt. 1), but in applying this method to other organic peroxides, linoxyn for example, which do not yield an acid to correspond to benzoic acid, the addition of sulphuric acid to the reaction mixture will be necessary.

(3) When the substance under examination dissolves readily in glacial acetic acid, no advantage is gained (*a*) by allowing the mixture to stand for 24 hours, (*b*) by heating the mixture above room temperatures, or (*c*) by cooling it.

EFFECT OF THE PRESENCE OF SULPHURIC ACID.—The low results obtained in the presence of increasing quantities of (*a*) concentrated sulphuric acid (Expts. 1–4) and (*b*) water (Expts. 9–10) are striking, and it is worthy of note in this connection that Baeyer and Villiger (*Ber.*, 1901, **24**, 740), using "angesäuerte Iodkaliumlösung" (no concentrations are mentioned) in the estimation of ethyl hydrogen peroxide, C_2H_5OOH, obtained only 21·07 per cent. of peroxide-oxygen, against a calculated value of 25·81 per cent. It might be supposed at first that excess of sulphuric acid produces low results by inhibiting the hydrolysis of the peroxide, but this supposition is untenable, because benzoyl peroxide liberates iodine directly in the absence of water, thus:

$$\begin{matrix} C_6H_5COO & KI \\ | & + \\ C_6H_5COO & KI \end{matrix} \longrightarrow 2C_6H_5COOK + I_2$$

without previously undergoing hydrolysis to benzoyl peracid, C_6H_5COOOH. This is shown by (i) Expt. 11, (ii) Expts. 13, 15, 16 (below) carried out in acetic anhydride solution, and (iii) the fact that addition of dry benzoyl peroxide and dry potassium iodide to sodium-dried alcohol or ether is followed in each case by immediate evolution of iodine (see also Gelissen and Hermans, *Ber.*, 1926, **59**, B, 63).

EFFECT OF WATER.—In order to decide, if possible, the effect of water on the course of the reaction a series of experiments was next carried out with acetic anhydride as solvent in place of glacial acetic acid. The former has the advantage of dissolving benzoyl peroxide more readily. The peroxide (0·2 grm.) was dissolved in 25 c.c. of the anhydride, and the solution treated as set out in Table II.

TABLE II.

Estimation of peroxide-oxygen content of benzoyl peroxide in *acetic anhydride* solution under different conditions.

Expt. No.	Amount of sulphuric acid added.	Amount of potassium iodide added. Grms.	Period of standing.	Temp.	Peroxide-oxygen found. Per Cent.
13	none	2 (solid)	10 minutes	Room	6·5
14	,,	2 in 2 c.c. water	,,	,,	6·6
15	,,	2 (solid)	1 hour	50° C.	6·3
16	,,	,,	24 hours	5°–10° C.	6·1
17	1 c.c. 98 per cent.	,,	,, ,,	,,	nil
18	,,	,,	1 ,,	50° C.	nil
19	1 c.c. 50 per cent.	2 in 2 c.c. water	24 ,,	5°–10° C.	2·5

Theoretical results were obtained by adopting the details already given in the case of glacial acetic acid. The reaction product must, however, in this case be vigorously shaken with water before the titration, since starch solution does not give a blue colour with iodine in the presence of much acetic anhydride.

It will be observed that addition of sulphuric acid, even in small quantity (Expt. 19; *cf.* Expt. 6), again leads to low results. The explanation of the cause

of this can now be obtained by making the following test-tube experiment, which shows that some or all of the liberated iodine is taken up by the acetic anhydride in the presence of potassium iodide, and that the peroxide itself is not concerned: A crystal of potassium iodide is heated with about 1 c.c. of acetic anhydride and a few drops of concentrated sulphuric acid; iodine is, of course, immediately liberated. The tube is cooled and its contents poured into about 50 c.c. of cold water. The iodine immediately disappears, and the solution does not yield a blue colour with starch, nor does a blue colour appear with addition of (*a*) more potassium iodide, (*b*) iodine-free hydriodic acid, (*c*) acetic acid, or (*d*) alkali. On addition of a considerable quantity of concentrated sulphuric acid an amorphous yellow precipitate slowly appears, which is very sparingly soluble in water, alcohol and ether. It evolves iodine on being heated or on being treated with concentrated sulphuric acid or chloroform, and it yields reactions for acetates and potassium. The yellow substance has not been analysed, but the conclusion seems justifiable that it is a compound of the type $x(CH_3CO)_2O.yKI.zI$, indications of the formation of which were obtained by Clover (*Amer. Chem. J.*, 1904, **31**, 256).

Succinyl Peroxide.—To ensure the general applicability of the method to straight-chain compounds some succinyl peroxide, $(COOH.CH_2.CH_2.COO)_2$, was prepared by the method of Clover and Houghton (*Amer. Chem. J.*, 1904, **32**, 55). The product was recrystallised twice from acetone, dried in a current of warm air, and the peroxide-oxygen content determined in glacial acetic acid solution. No sulphuric acid was added, and the liberated iodine was titrated after shaking for a few minutes with the potassium iodide solution. The result was 6·7 per cent., against a calculated value of 6·8 per cent. Clover and Houghton (*loc. cit.*) obtained 6·7 per cent., using water as solvent.

Alcohol, Acetone, etc., as Solvents.—Gelissen and Hermans (*loc. cit.*) estimate benzoyl peroxide by dissolving 0·2 grm. of the sample in 10 c.c. of acetone, adding 3 c.c. of concentrated aqueous solution of potassium iodide, and titrating the liberated iodine immediately with $N/10$ sodium thiosulphate solution. We have confirmed the accuracy of this method, no sulphuric acid being added. Ordinary technical acetone also gives theoretical results (6·6 per cent.), but in this case a blank experiment must also be made. Estimations can also be carried out in solutions in alcohol (both 99 per cent. and 95 per cent.); no blank is required in this case, but a comparatively larger quantity of the solvent (about 100 c.c.) is required for 0·2 grm. of the sample. Ether and carbon tetrachloride are unsatisfactory as solvents for the purpose, both in the cold and on heating.

Oxidised Oil.—Estimation of the peroxide-oxygen content of a sample of oxidised linseed oil was then examined. The sample was prepared by bubbling oxygen through the oil until the nett increase in weight was 4·03 per cent. Concordant results, namely, 2·2 per cent. of peroxide-oxygen, were obtained by adopting the following procedure: About 1 grm. of the oil is weighed and dissolved in 25 c.c. of glacial acetic acid contained in a glass-stoppered bottle. To the solution are added (i) 1 c.c. of approximately 50 per cent. sulphuric acid ("A-R."), and (ii) 2 c.c. of cold saturated potassium iodide solution ("A-R"). The stopper

of the bottle is wetted with dilute potassium iodide solution. The mixture is then allowed to stand in the dark for 24 hours at room temperature, after which it is diluted with about 100 c.c. of distilled water and titrated with $N/10$ sodium thiosulphate solution. At the same time, in bottles of the same shape and size, the following tests are made:—(i) with a benzoyl peroxide control, and (ii) two blanks.

About 20 experiments were carried out in which the following factors were separately varied: (*a*) The quantity of sulphuric acid added; (*b*) the duration of the experiment; (*c*) the temperature.

(*a*) If concentrated sulphuric acid is employed the oil undergoes charring and the result is low. If, on the other hand, the acid employed is much below 50 per cent. concentration the oil is partially thrown out of solution, and the result is again low.

(*b*) If for any reason it becomes necessary to continue the duration of an estimation for more than 24 hours, an oxygen-free atmosphere must be provided, because with long exposures, say 48 hours, the blanks give very discordant figures, although the bottles may be of the same size and shape. This explains also why *two* blanks are recommended, even when the exposure is only 24 hours. The average of the two readings obtained with the blanks is deducted from the titration figure. Some typical readings of the volume of $N/10$ sodium thiosulphate run into the blank mixtures of glacial acetic acid, sulphuric acid and potassium iodide were: (i) 4·25, (ii) 4·35, (iii) 4·45 c.c.

(*c*) No advantage is gained by keeping the bottles in an ice-box, and discordant figures result by warming in a water-bath to 50° C.

The above modified Fahrion method has been used with success in the examination of a large number of complex compounds of oily and gummy consistency which were obtained by the oxidation of vegetable oils. It should be noted, however, that the method must be used with caution in the case of those substances (*e.g.* raw drying oils) which absorb iodine directly from glacial acetic acid solution, as low results would then be obtained. Direct absorption of iodine by drying oils in this manner is, however, slow, and after 24 hours' contact usually corresponds to an iodine value of approximately 25, as compared with a true iodine value of about 170.

A few values of general interest are set out in the Table below:

TABLE III.

	Substance.	Peroxide-oxygen. Per Cent.
1.	Linseed oil (heat thickened)*	0·7
2.	Do. (blown)*	1·6
3.	Wood oil (blown)*	3·4
4.	Do. (exposed for 18 months)* ..	6·3
5.	Oxidised glyceride from wood oil† .. .. (glyceride of β-elaeostearic acid)	4·5–4·9
6.	Portion of (5) insoluble in petroleum spirit† ..	3·0–3·2

* A correction was made in these cases for the iodine which was absorbed by the oil, by ascertaining separately the effect of addition of the quantity of oil employed in the determination on a benzoyl peroxide blank experiment.

† Morrell and Marks (*loc. cit.*).

SUMMARY.—The effects of various conditions on the determination of the peroxide-oxygen content of organic peroxides have been investigated. Modified conditions have been put forward for the determination of the peroxide-oxygen content of oxidised oils and their decomposition products.

Our thanks are due to Messrs. Mander Bros., Ltd., Wolverhampton, in whose laboratory part of the above work was carried out.

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DISCUSSION.

The PRESIDENT wondered why sulphuric acid was necessary at all in the presence of so much acetic acid, since some of the experiments without sulphuric acid seemed to have given satisfactory results.

Dr. H. E. COX suggested that if iodine were really absorbed by glacial acetic acid, it would be decomposed again on the addition of water.

Mr. J. R. NICHOLLS said that the difficulty in the titration of peroxides was the lag in the liberation of the iodine due to the presence of water. He suggested that in the case of an oil dissolved in a large proportion of solvent, the solvent might be oxidised before the oil.

Mr. S. MARKS, replying, said that with regard to the addition of sulphuric acid—he took it that when sulphuric acid was added potassium iodide was decomposed and the function of the sulphuric acid was to take up the potash. In the case of oils he had certainly found that a small quantity of sulphuric acid (say 1 c.c. of 50 per cent.) was advisable—otherwise one did not get good results. He did not see how one could apply a correction for the absorbed iodine; when one determined an iodine value there was no sulphuric acid, and the two figures were not obtained under the same conditions. The average of the two blanks had been taken in order to avoid the discrepancy obtained in the titration of iodine after the use of glacial acetic acid and a saturated solution of potassium iodide. Answering Dr. Cox, Mr. Marks said that the addition of water did not effect decomposition. With regard to the formation of blue colour, when he failed to get a blue colour he added to the reaction mixture quite a number of substances with a view to "coaxing" it. When iodine had disappeared from view by the addition of water, he found that the blue colour did not appear with potassium iodide, iodine-free hydriodic acid, more acetic acid or more alkali, and he felt that the possibility of iodine being there and not showing was rather remote.

Electrometric Determination of Copper.

I. MÜLLER AND RUDOLPH'S METHOD.

BY MARJORIE E. PRING, M.Sc., AND
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GRAVIMETRIC methods of determining copper, with the exception of Rivot's thiocyanate process, are troublesome to carry out, and on occasion may be very inaccurate. Consequently, volumetric methods of determination are usually employed. Difficulties frequently occur in the volumetric determination of copper when highly coloured solutions, or solutions containing other metals have to be used. We have, therefore, investigated the existing volumetric methods for the determination of copper using electrometric methods of ascertaining the end-point of the titration, and, in addition, we have examined several possible new methods in the same way. Electrometric titrations, in addition to other advantages, allow one to carry out determinations in highly coloured and even in turbid solutions, and frequently in the presence of metals other than that being determined.

A considerable amount of work on the electrometric determination of copper has been published, but a careful study of the results obtained by these methods does not suggest an entirely satisfactory process for the electrometric determination of copper.

PRECIPITATION OF INSOLUBLE COPPER COMPOUNDS.—In 1911 Dutroit and von Weise (*J. Chim. Phys.*, 1911, **9**, 608) investigated the titration curves obtained during the precipitation of insoluble copper compounds by various reagents. The process as a method for the determination of copper was unsuccessful unless a polarised copper electrode was used. In the case of the precipitation of hydroxide, ferrocyanide, thiosulphate, iodide, phosphate and thiocyanate either a poor end-point was obtained in the titration or the curves were irregular. The only precipitation giving good results was that of the sulphide, but even this did not yield an accurate end-point. The titration of solutions of copper salts was further investigated by Hedrich (*Diss.*, Dresden, 1919), and from his results it may be taken that the method is unsuitable for general use. Oesterheld and Honegger (*Helv. Chim. Acta*, 1919, **2**, 238) investigated the electrometric titration of iodine, liberated by the action of potassium iodide on cupric salts, by means of sodium thiosulphate. Their experiments show that a sharp end-point can be obtained, but their work deals mainly with the effect of sulphuric acid of varying concentration on the course and result of the titration.

TITRATION WITH TITANOUS SALTS.—Several accounts have been published of the electrometric determination of copper by titration with solutions of titanous salts. Thus Zintl and Wattenberg (*Ber.*, 1922, **56**, 472) add an excess of titanous

chloride to the solution of the copper salt and titrate the excess with either potassium bromate or potassium dichromate. Willard and Fenwick (*J. Amer. Chem. Soc.*, 1923, **45**, 933) in a short note state that solutions of cupric salts may be titrated directly with titanous sulphate with good results if a bimetallic electrode system is used. Tomiček (*Rec. Trav. Chim.*, 1924, **43**, 798) investigated the direct titration with titanous chloride and found that the results were always about 1·0 per cent. too high, but in the presence of potassium iodide or potassium thiocyanate, both of which precipitate the cuprous salt formed in the reaction, good results could be obtained. When tartrates or tartaric acid are present good results can be obtained only in the presence of potassium iodide; the presence of potassium thiocyanate has a disturbing effect on the reaction. Zintl and Rauch (*Z. anorg. Chem.*, 1925, **146**, 281; *Z. Elektrochem.*, 1925, **31**, 428) reinvestigated the indirect method of oxidising the excess of titanous salt with potassium bromate and confirm the previous results of Zintl and Wattenberg. They maintain that the method is very accurate. The high results obtained by Tomiček in the direct titration with titanous chloride are attributed to the presence of dissolved oxygen in the copper sulphate solution. To remove this error they suggest either boiling the solution in an atmosphere of carbon dioxide before titration or adding a few drops of titanous chloride solution and oxidising the excess with potassium bromate or potassium dichromate. Kolthoff, Tomiček and Robinson (*Z. anorg. Chem.*, 1926, **150**, 157), on repeating Tomiček's experiments, find that the results of direct titration are consistently 0·2–1·2 per cent. too high. The best results are obtained when correction is made for the dissolved oxygen, as stated above, but the process is troublesome. The fall in the E.M.F. at the end-point is not very pronounced, and even when the correction for dissolved oxygen is made the accuracy is not great. Further, it is found that the presence of a trace of copper sulphate in the titration of dichromate with titanous chloride raises the titre 0·2 per cent. This point in itself tends to vitiate the results obtained by the indirect method of estimating copper. In a reply to this criticism Zintl (*Z. anorg. Chem.*, 1926, **152**, 35) suggests that Kolthoff, Tomiček and Robinson used unsatisfactory methods to standardise their titanous chloride solution. He again points out the necessity for removing dissolved oxygen from the solution, and he insists that an error of 0·2 per cent. is not greater than the errors in other methods used by these authors. He further states that the method always gives a sharp end-point. The determination of copper by reduction of the cupric salt has also been investigated by Bucherer and Schupp (*Ind. Eng. Chem.*, 1926, **18**, 121). They titrated cupric salts directly with stannous, titanous and chromous chlorides, respectively; also excess of these reagents was added to the cupric salt, and the excess titrated with potassium dichromate solution. Direct titration with stannous chloride and titanous chloride gave high results, whilst that with chromous chloride gave good results if the value taken was the mean of the values calculated from the titrations represented by $Cu^{\bullet\bullet} \longrightarrow Cu^{\bullet}$ and $Cu^{\bullet} \longrightarrow Cu$. In those cases where an excess of the reducing agent is added and the excess titrated back with potassium dichromate it was found that good results were obtained with chromous chloride, but with titanous

chloride the values were too high, whilst with stannous chloride the method is impracticable, for both the cuprous compound and the excess of stannous chloride are oxidised. Müller and Adam (*Z. Elektrochem.*, 1923, **29**, 49) attempted to determine the concentration of a cupric salt by adding to it an excess of potassium cyanide and titrating the excess with silver nitrate, using a silver electrode. Trustworthy results were not obtained, since the reduction of the cupric compound to a cuprous compound only approaches completion when the solution is submitted to prolonged heating, and this affects the concentration of the potassium cyanide. Müller and Rudolph (*Z. anal. Chem.*, 1923, **63**, 103) investigated the method of reducing a solution of a cupric salt by sodium bisulphite, heating to 70° C., and then titrating with potassium thiocyanate, using a copper electrode. They state that this process gives results too low by a constant 0·7 per cent. if the conditions are well controlled.

From what has been said it will be clear that none of the methods proposed for the electrometric determination of copper is generally applicable and reliable.

Experimental.

The titrations described were made by means of an apparatus designed by Spencer (*J. Soc. Chem. Ind.*, 1927, **46**, 423T), the voltmeter of which could be read to 0·001 volt. The burettes, flasks and pipettes were carefully calibrated, and the materials used were chemically pure. The copper sulphate solutions were prepared from accurately weighed quantities of A.R. material, and the concentration was confirmed by electrolysis. In all cases the solution was mechanically stirred during the titration.

Investigation of Müller and Rudolph's Method.—The determination was first carried out, following exactly the instructions given by Müller and Rudolph (*loc. cit.*). To 10 c.c. of a 0·1 *m* solution of copper sulphate 20 c.c. of a 5 per cent. solution of sodium bisulphite and 70 c.c. of water were added. The solution was heated to 70° C., a copper electrode and a 0·1 *N* calomel electrode inserted, and the hot solution titrated with a 0·1 *N* solution of potassium thiocyanate. The E.M.F. of the cell, Cu | $CuSO_4$soln. | 0·1 *N* KCl.Hg_2Cl_2 | Hg, was measured one minute after each addition of thiocyanate, and the E.M.F. values plotted as ordinates, against the number of c.c. of titrating liquid added, as abscissae, and a titration curve drawn.

The type of curve obtained is shown in Fig. 1; it will be seen that a rise in the E.M.F. occurs at the end-point, which is sufficiently marked to enable the position to be determined within 0·05 c.c. It was found, however, that the titration is difficult to control, and the results obtained do not agree well. Various factors, including the time taken for the addition of the thiocyanate, the temperature and the amount of bisulphite used, appeared to influence the end-point; consequently each of these factors has been separately investigated. Further, it was found that the sharpest end-point was obtained when the copper electrode consisted of a piece of electrolytic copper which had been washed with dilute nitric acid, followed by distilled water, immediately before use.

Influence of Temperature.—Series of titrations were carried out, as described above, at 65° C., 70° C., and 75° C. A solution of copper sulphate (I) containing

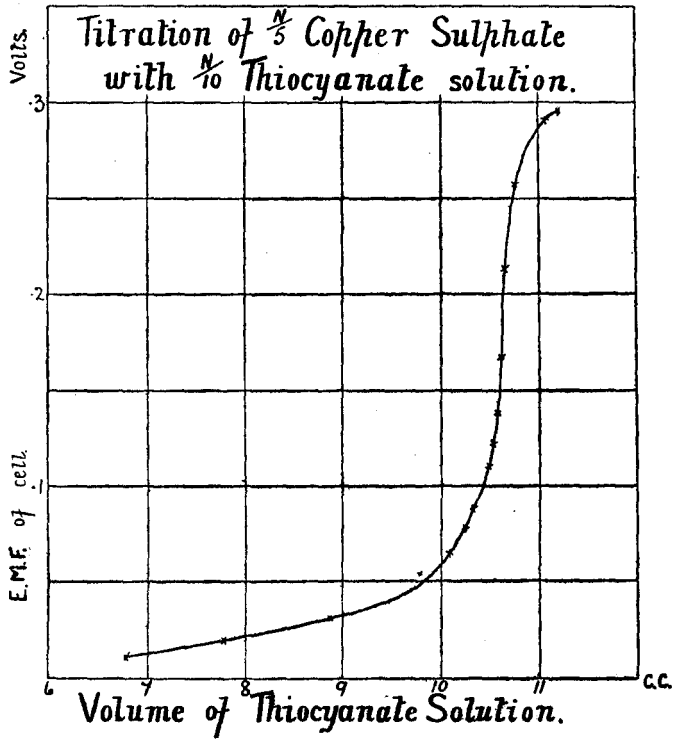

FIG. 1.

24·940 grms. per litre was titrated with 0·1036 *N* potassium thiocyanate solution, which had been standardised against 0·09932 *N* silver nitrate solution.

9·97 c.c. $CuSO_4$ solution (I) + 20 c.c. $NaHSO_3$ (5 per cent. solution) + 70 c.c. H_2O

65° C.		70° C.		75° C.	
KCNS added. c.c.	E.M.F. Volts.	KCNS added. c.c.	E.M.F. Volts.	KCNS added. c.c.	E.M.F. Volts.
9·00	0·048	9·00	0·050	8·99	0·050
9·24	0·058	9·10	0·059	9·13	0·060
9·35	0·071	9·22	0·068	9·26	0·080
9·46	0·091	9·38	0·095	9·34	0·100
9·58	0·120	9·47	0·115	9·38	0·115
9·62	0·149	9·51	0·128	9·43	0·139
9·66	0·199	9·55	0·140	9·47	0·159
9·70	0·230	9·59	0·178	9·51	0·182
9·74	0·241	9·63	0·218	9·56	0·198
		9·67	0·225		
End-point = 9·64		End-point = 9·61		End-point = 9·47	

Theoretically, 9·97 c.c. of copper sulphate solution require 9·61 c.c. of potassium thiocyanate solution. In the case of the titration at 75° C. the solution became brown and turbid before the titration was begun, the end-point was not sharp, and the voltmeter reading was not steady.

A second series of experiments was made with copper sulphate solution (II), which contained 6·336 grms. of copper per litre; this was titrated with 0·0923 *N* potassium thiocyanate solution.

Temperature ..	65° C.	70° C.	75° C.
End-point ..	10·58 c.c.	10·53 c.c.	10·35 c.c.

10 c.c. of $CuSO_4$ solution (II) require theoretically 10·37 c.c. of 0·0923 *N* KCNS.

The results show that a small rise in temperature above 70° C. makes a large difference in the results; thus there is a difference of about 1·5 per cent. between the values at 70° C. and 75° C.; on the other hand, the difference between the titre at 65° C. and 70° C. is small, about 0·3 per cent. At temperatures above 75° C. the end-point is difficult to determine, since the change in E.M.F. is small.

Influence of Time.—The effect of changing the time factor was examined, using copper sulphate solution (I). The mixture was prepared as in the previous cases, heated to 70° C., and kept at this temperature for a definite time before commencing the titration. The electrodes were then inserted, and the thiocyanate run in almost to the end-point, which was then found by taking voltmeter readings one minute after the addition of each drop.

9·97 c.c. $CuSO_4$ solution (I) + 20 c.c. $NaHSO_3$ (5 per cent. solution) + 70 c.c. H_2O.

Heated for 1 minute.		Heated for 5 minutes.	
KCNS added. c.c.	Voltage.	KCNS added. c.c.	Voltage.
9·00	0·050	9·01	0·054
9·10	0·059	9·29	0·090
9·22	0·068	9·31	0·108
9·38	0·095	9·36	0·121
9·47	0·115	9·40	0·150
9·51	0·128	9·44	0·189
9·55	0·140	9·48	0·219
9·59	0·178	9·52	0·231
9·63	0·218		
9·67	0·225		
End-point 9·61		End-point 9·42	

The correct end-point lies at 9·61 c.c. In the case of the solution which has been allowed to stand for 1 minute the solution is green and clear when the titration is begun, and the precipitate is white, whilst the solution kept for 5 minutes at 70° C. is turbid and brown before titration, and the precipitate is slightly coloured. Further, the voltmeter needle drifts in the experiments made with solutions which have been kept for 5 minutes, so that the readings are difficult to take. There is a difference of 1·9 per cent. between the values of the two solutions. A comparison of the titration curves (Fig. 2) will make it clear that the end-point is much sharper for the solution kept the shorter time at 70° C.

Experiments were next made in which the voltmeter was allowed to settle before the reading was recorded and more thiocyanate added. This process was found to be impracticable, for, as the end-point is approached, it was found that

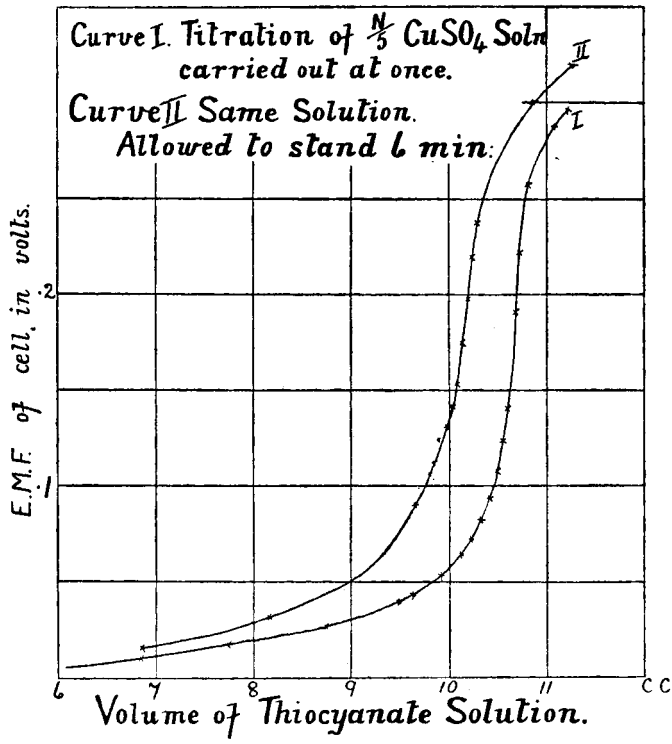

FIG. 2.

after each addition of thiocyanate the E.M.F. rises slowly for a while and then drifts back. Consequently the maximum voltmeter reading was recorded, and the following results obtained at 70° C.

9·97 c.c. $CuSO_4$ solution (I) + 20 c.c. $NaHSO_3$ (5 per cent. solution) + 70 c.c. H_2O.

KCNS added. c.c.	Voltage.
9·01	0·039
9·09	0·048
9·24	0·074
9·34	0·092
9·42	0·118
9·46	0·129
9·50	0·150
9·54	0·170
9·58	0·200
9·63	0·220
9·67	0·232

End-point 9·56

KCNS added. c.c.	Voltage.
8·99	0·051
9·11	0·071
9·27	0·091
9·37	0·114
9·42	0·130
9·47	0·145
9·51	0·162
9·56	0·190
9·61	0·211
9·67	0·219

End-point 9·54

The end-point is poor in this case, and has a value 0·07 c.c., or 0·62 per cent. lower than the correct value, 9·61, obtained by reading the voltmeter one minute after each addition.

Influence of Concentration of Bisulphite.—To examine this point titrations were made with copper sulphate solution (I) at 70° C., using various amounts of

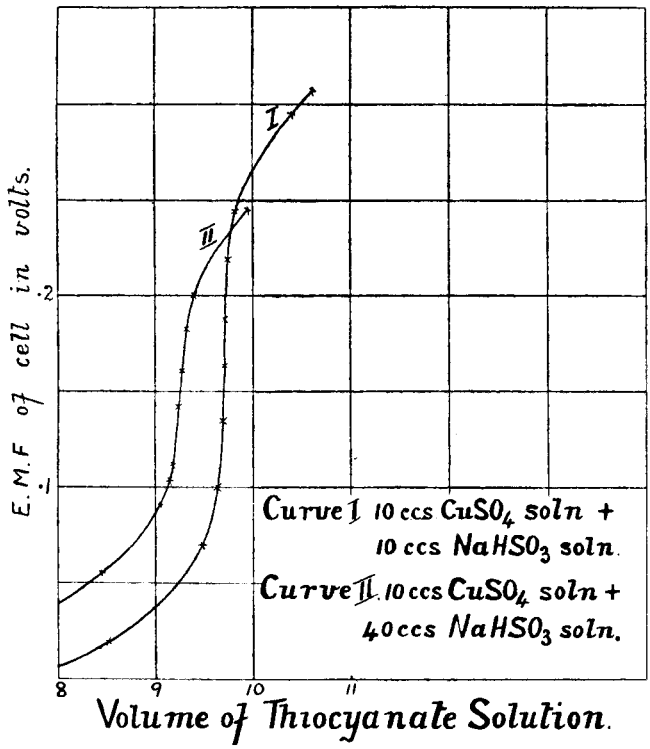

FIG. 3.

bisulphite in 5 per cent. solution, and the total volume was made up to 100 c.c. with distilled water.

9·97 c.c. $CuSO_4$ solution (I) + $NaHSO_3$ (5 per cent. solution) + water.

Volume of 5 per cent. $NaHSO_3$ solution ..	10 c.c.	20 c.c.	40 c.c.
Titration value	9·70 c.c.	9·61 c.c.	9·28 c.c.

The solution was clear and green before the titration was begun, when the lowest concentration of bisulphite was used, and the end-point, as seen in the curves (Fig. 3), is sharp, but it is almost 1·0 per cent. too high, whilst with the most concentrated bisulphite the solution becomes brown and turbid before the titration is begun and the end-point is poor (Fig. 3), whilst the titre is about 3·5 per cent. too low.

DISCUSSION.—The results of this investigation show that Müller and Rudolph's method of electrometric titration of copper is very sensitive to changes of temperature, concentration of bisulphite, and time taken for the operation; hence it

becomes exceedingly difficult to state how far it will furnish accurate results. A comparison of the calculated results with those obtained when the directions of Müller and Rudolph are closely followed gives the following figures.

	Vol. KCNS (calc.). c.c.	Vol. KCNS (exptl.). c.c.
$CuSO_4$ solution (I) ..	10·37	10·53
$CuSO_4$ solution (II) ..	10·61	10·61

These show clearly that there is no constant error which can be used as a correcting factor, as claimed by Müller and Rudolph. The possibility of obtaining concordant results appears, therefore, to be remote. The results are highest when the temperature is below 70° C., when the solution is titrated as quickly as possible, and when the concentration of the bisulphite is low. Müller and Rudolph attribute their high results to the adsorption of the thiocyanate ion by the precipitate. It appears, however, more probable that they are due to the incomplete reduction of the cupric salt by the bisulphite. In all cases where high results were obtained in the present work the solution was green at the start of the titration and, in consequence, a small quantity of thiocyanate must be used in completing the reduction. When the results are low, that is, when the temperature is above 70° C., or when the solution is kept for a few minutes before the titration is begun, or when a high concentration of bisulphite is used, the solution becomes brown and turbid. In some cases a reddish precipitate is produced, which varies in composition and is evidently the substance described by Chevreul (*Ann. Chim. Phys.*, 1812, (i), **83**, 181). This precipitate contains cupric cuprous sulphite, and its presence in the titration liquid indicates that some of the copper is removed from the solution as sulphite, and consequently that the amount of thiocyanate used must be too low.

A number of experiments were made in which sulphur dioxide was used in place of sodium bisulphite as reducing agent; this prevented the formation of an insoluble complex compound, but the reduction was incomplete, even on boiling. The titration curves show that the end-point is sharpest when the solution does not become turbid before the titration is begun and when the temperature is not allowed to rise above 70° C., but in no case can the process be regarded as satisfactory. The conditions must be exactly regulated to obtain concordant results, and new conditions must be established for varying copper concentrations if reliable results are to be obtained. Consequently the process becomes tedious, time-consuming, and of little practical value.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research enabling one of us (M.E.P.) to take part in the work.

Bedford College,
University of London.

Apparatus for the Analysis of Small Samples of Gas.

By H. R. AMBLER, B.Sc., A.I.C.

(*Read at the Meeting, May 1st,* 1929.)

The simple apparatus here described has been evolved, primarily, for the analysis of samples of gas of about 1 c.c. Samples of this magnitude can be analysed with an accuracy of about 1 per cent.

Where larger samples for analysis are available (*i.e.* 15 c.c.), an accuracy of about 0·1 per cent. is obtainable with a minimum of manipulation.

Introduction.—In the analysis of samples of gas of about 1 c.c., causes of error become important, which would be quite negligible for larger samples. The chief of these are:—

(1) Rubber connections, which may lead to (*a*) small air-locks at the joints, (*b*) small leaks when the rubber becomes old.

(2) Physical solution of the constituent gases in each reagent, as distinct from the specific chemical absorption for which the reagent is used.

(3) The limiting error of reading, which is proportionately greater for smaller samples.

The present apparatus has been designed to reduce such effects to a minimum: (1) Rubber connections have been abolished. (2) The volume of absorbent reagent has been diminished. (3) The sensitiveness of reading has been increased.

Apparatus and Procedure.—A diagrammatic sketch of the apparatus is given in Fig. 1.

It consists essentially of two three-way taps, T_1T_2, connected with the glass bulbs C and B, respectively, and joined together at their "one-way" ends.

The experimental procedure is as follows:

(1) The gas sample is introduced into the bulb B from A. The way this is done depends on the vessel in which the sample is received. Where possible, it is convenient for this to be fitted with a capillary three-way tap, with the "common" end uppermost. This is joined to A by rubber tubing, and air driven out of the connection with mercury from the apparatus. If, however, as is frequently the case, the sample is contained in an inverted test-tube, it may be transferred to the apparatus by means of a capillary U-tube, one end of which is connected with A by rubber tubing, and the other end, which should be drawn out, inserted under the test-tube in a mercury-jar, after air has been driven out by means of mercury.

(2) The gas sample is transferred to C and measured. This is done by measuring the pressure at which the constant volume of bulb (or bulbs) is filled. The pressure is measured on a mercury manometer, M_1. By running mercury beyond the tap T_1, to a marked point F, C is sealed against any leak out of gas or leak in of air during the pressure measurement. It may be convenient, when the highest accuracy is not required, for this point F to be taken on the horizontal part of the tube, instead of on the vertical (water-jacketed) part, as shown in the diagram.

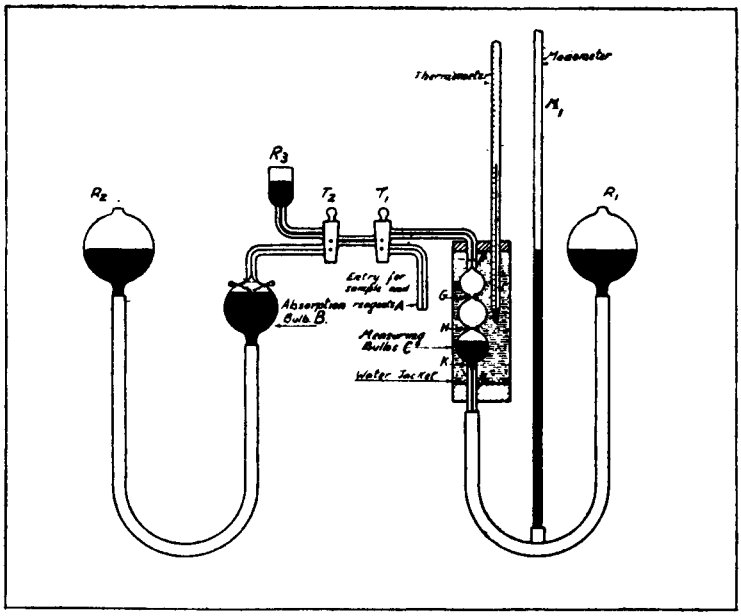

FIG. 1.

(3) A quantity of the appropriate absorbent, equal in volume to about half that of the gas sample, is introduced into B from A.

(4) The gas is transferred to B, where the absorption takes place.

(5) The gas is transferred back to C and again measured. Immediately the gas has passed T_2 the latter is reversed, and the gas followed up by mercury from R_3 to the mark F as before.

The measuring vessel C consists of three bulbs, one, two, or three of which can be used according to the magnitude of the gas sample. In this particular apparatus their volumes are 1, 3 and 6 c.c. respectively. Horizontal marks G, H, K are etched below each bulb. Gas samples, of magnitude ranging from about 0·25 to 15 c.c. (at N.T.P.) can be dealt with. A water jacket fitted with thermometer surrounds the measuring bulbs.

The absorption bulb B is fitted with platinum electrodes and spark gap, or a platinum spiral, or both. The volume of B is about 25 c.c.

The connecting glass tubes are made of capillary tubing of 1 mm. bore.

The manometer is attached to a silver-backed glass scale, 1 metre in length, graduated in mm. This need not be placed inconveniently close to the rest of the apparatus, but may be mounted on a neighbouring wall or other suitable place.

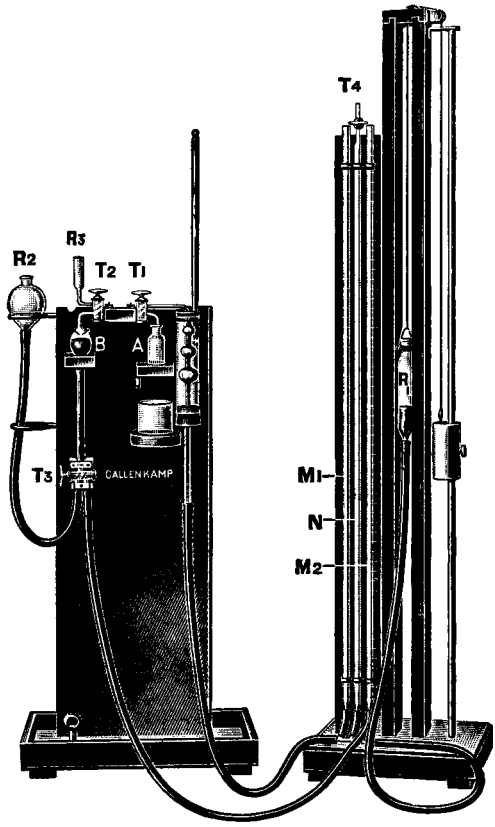

FIG. 2.

The central glass part of the apparatus, with its wooden stand, may then be gently shaken in order to agitate the absorbent solution. Very slight movement gives adequate agitation of the liquid. Reading is very easy and parallax is avoided.

There are none of the difficulties of levelling that are found with the constant-pressure types of apparatus. Manipulation is simple and rapid. A gas of 6 constituents (say CO_2, O_2, CO, CH_4, H_2, N_2) can be analysed within half an hour.

The size of that part of the apparatus in which the gases are manipulated is quite small, *i.e.* 9″ × 9″ × 1″. It is simple and strong. The amounts of mercury and of reagents are small. The complete apparatus is shown in Fig. 2.

REDUCTION OF ANALYSES.—Let K be the reading on the manometer when the measuring bulbs are filled at atmospheric pressure. This is determined once and for all by connecting them with the atmosphere, through T_1 and T_2, with R_3 empty, and bringing the mercury to the appropriate mark. (If at any time it is feared that the level of the bulbs relative to the scale can have changed, this can be checked by the same procedure). K is not necessarily level with the mark on the bulb, as the bore of the tube at the mark may not be the same as that of the manometer. By determining K as above, however, capillarity effects are eliminated, provided the bore of the manometer tube is uniform.

Let A be the reading on the manometer at the beginning of the analysis,

Then P, the pressure in the bulbs,

$$= B + A - K, \text{ where B is the barometric pressure.}$$

The bulbs are washed out with water between analyses; hence the gas is always saturated with water vapour. The partial pressure of the gas under analysis is then:—

$$B + A - K - W,$$

where W is the vapour pressure of water at the temperature indicated by the thermometer in the water-jacket.

If V be the volume of the bulbs, then the volume of a sample at N.P. is:—

$$V \times \frac{B + A - K - W}{76}$$

If the manometer reading after absorption of, say, CO_2 be A′, the volume of gas at N.P. now is:—

$$V \times \frac{B + A' - K - W}{76}$$

The volume of CO_2 absorbed is, then:—

$$\frac{V(A - A')}{76}$$

The percentage of CO_2 is:—

$$\frac{A - A'}{B + A - K - W} \times 100.$$

The quantity (B + A − K − W), representing the original pressure of the gas sample, is determined once for each analysis. The percentage of each constituent is directly proportional to a difference of readings on the manometer.

BAROMETER ATTACHMENT.—Analysis requires a knowledge of the barometric pressure. A barometer may be incorporated in the apparatus as follows (see Fig. 2). By the side of the manometer, M_1, is placed a second tube, N, of the same bore, and connected at its lower end with M_1 and R_1. The upper end is fitted with a capillary tap, T_4. If R_1 is raised so as to drive mercury past T_4, the latter closed, and then R_1 lowered to some position lower than T_4 by more than the barometric height, the space below T_4 will be a Torricellian vacuum, and the barometric pressure will be equal to the difference in the heights of mercury in this tube and in M_1. A barometer reading can be so taken at any time during an analysis. If a drying tube is attached to T_4, and the latter occasionally left open, the space above the mercury is kept free of water vapour. Normally, the reservoir

is sufficiently high for the barometer tube to be completely filled with mercury. If a leak past T_4 is suspected, R_1 can be raised at any time, and the mercury taken past the tap immediately before reading.

USE OF PRESSURE GAUGE.—It may sometimes be convenient and more speedy, when high accuracy is not required, to read the pressure of the gas on a dial instead of on a mercury manometer. For a portable apparatus this would present considerable advantages.

An atmospheric gauge, has been used in conjunction with the mercury manometer. The gauge was used filled with alcohol, and the level of the mercury and alcohol interface kept constant within very small limits by making its area large, *i.e.* about 50 sq. cm. This was done by causing it to occur in the middle of a large bulb.*

An analysis was carried out, in which readings were taken both on the manometer and on the pressure gauge, and the results from the two sets of readings calculated independently. The figures agreed within 1 per cent. For many purposes, sufficient accuracy could be obtained with the gauge alone.

AUXILIARY MANOMETER.—It is sometimes desirable, particularly in the case of absorptions that take several minutes for completion, to be able to observe the progress of the reaction without having to transfer the gas to and from the measuring bulbs.

For this purpose, an auxiliary manometer M_2 is connected with the absorption bulb B through a three-way tap, T_3, which, in its normal position, connects B with the reservoir R_2. If, after gas has been introduced into B, this tap is reversed, it connects B with M_2 and cuts off R_2. The progress of absorption of gas in the (approximately) constant volume above the absorbing solution in B can then be followed on the manometer M_2.

PRECAUTIONS IN USE.—As with all types of apparatus, reagents must not be allowed to enter the measuring-bulbs, as their presence in any appreciable quantity may lower the aqueous vapour-pressure in the bulbs.

The portion of capillary tubing between the taps T_1 and T_2 becomes wetted with reagents; it is possible to wash this out between absorptions, by running water from R_3 to A. This is found, however, to be in general unnecessary, since any gas which might thus come in contact with the reagent has already been in contact with the same reagent.

After exploding for hydrogen and methane (and also before a fresh analysis), the absorption bulb should be washed free of alkali. This is conveniently done by washing out once with weak sulphuric acid and then with water, introduced at "A" in the same way as the absorbent reagents, the gas being retained meanwhile in the measuring bulbs. It is advisable at the same time to wash out the measuring bulbs with water, in case any minute traces of alkali had entered them. The washing may be done without loss of gas or admission of air, by drawing a small quantity of water into bulb B, and transferring it to the measuring bulbs in the presence of the gas sample. (If acid has not been washed out of B, some will be carried into the measuring bulbs and may react with traces of carbonates, producing carbon dioxide, affecting the methane figure.) This procedure eliminates

* This would be unnecessary with an all-steel gauge, which could be filled with mercury.

the necessity of a separate washing of the gas with water after absorption of carbon monoxide with ammoniacal cuprous chloride.

For suggestions and useful discussions, I am indebted to Mr. T. Carlton Sutton, M.Sc., with whose approval the apparatus has been developed.

RESEARCH DEPARTMENT,
WOOLWICH.

DISCUSSION.

The PRESIDENT remarked that Mr. Ambler had now taken from the gas analyst the possibility of saying that the sample was too small for analysis. He wished to express his very great appreciation of this paper, particularly of the trouble Mr. Ambler had taken in bringing the apparatus itself to the meeting.

Mr. T. C. SUTTON said that he had been closely concerned with the development of this instrument; such constructive ideas as he had been able to put forward had already been incorporated in it, and he would not detail them here ; he had specially welcomed it, since the results of even rapid analyses made with it were accurate, and he could no longer be told that there was "insufficient sample." An analysis to one part in 500 could be made very quickly, and he thought that this, coupled with the fact that this was a simple apparatus which could be kept clean easily, was an important advance in gas analysis. He would like to point out that here was an instrument which, while being as good as any other for the analysis of large samples of gas, could be used without alteration as a sensitive and accurate instrument for micro-analysis. If required, the instrument could be made portable, and so could be taken to mine-heads, etc., when it was necessary to analyse gases on the spot.

Mr. G. N. HUNTLEY said that about 25 years ago he had devised an apparatus which had some resemblance to this one, and it had been described by Travers.

Mr. AMBLER, replying to Mr. Huntley, said that an instrument such as this embodied a number of separate principles; originality was not claimed for each separate part. The present form of the apparatus was the result of extensive adaptations and alterations that had been found useful in his daily work.

A Method for the Separation and Determination of Arsenic.*

By B. S. Evans, M.C., Ph.D., F.I.C.

Most of the methods for the determination of arsenic in metals are based on its distillation as trichloride; the majority of the remainder depend on its precipitation as sulphide; sometimes the two processes are combined. Whilst both of these processes are excellent they have drawbacks, some of which are not always realised. The distillation method, besides the obvious disadvantage of requiring special apparatus, is quite capable of giving low results unless carried out with great caution; it requires the arsenic to be in the reduced condition; where the solution of the sample and distillation of the arsenic are carried out in one operation special solutions are required (*e.g.* strong ferric chloride, calcium chloride and hydrochloric acid solution), which may be exceedingly difficult to prepare free from arsenic, and it is almost impossible also to test the accuracy of these methods; a "blank" is usually involved; in the presence of large amounts of antimony distillation methods become decidedly unsafe unless subsequent separation from antimony in the distillate is resorted to. The sulphide precipitation, at best, is tedious, especially if, as is sometimes recommended, a second precipitation has to be carried out; it is attended also with all the dangers of colloid precipitation, which can be serious, especially among sulphides; it does not lend itself readily to subsequent volumetric determination, a drawback where small amounts are concerned. For the rest, the magnesium pyroarsenate determination is very apt to give low results owing to the solubility of the precipitate, whilst Bettendorf's reagent, though apparently capable of giving good results, requires inordinately long periods of digestion, etc.

Precipitation by Hypophosphorous Acid.—The precipitation of metallic arsenic by hypophosphorous acid first described by Thiele (*Annalen*, 1890, **263**, 361), and applied by Bougault to the determination of cacodylic acid, was the subject of a paper from the analytical point of view by Engel and Bernard (*Compt. rend.*, 1896, **122**, 390); this paper was purely academical, and did not deal at all with the problems involved in the separation of arsenic from commercial materials. Brandt in 1913 and 1914 published a series of papers (*Chem. Ztg.*, 1913, **37**, 1445, 1471, 1496; 1914, **38**, 295, 461, 474) on the application of the method to the determination of arsenic in metals; these papers escaped my notice until after the completion of the present work; moreover, part of Brandt's method and some of his conclusions seem open to criticism, and, in any case, the method does not appear to be used in this country. This paper must therefore be regarded as reopening the subject with fresh data and, to a certain extent, fresh technique. Criticism of Brandt's

* Communication from the Research Department, Woolwich.

method and findings will be reserved till the end. The hypophosphorous acid reduction has much to recommend it from an analytical standpoint.

(*a*) It has considerable delicacy (0·4 c.c. of $N/100$ As_4O_6 = 0·00015 grm. of As), gives a precipitate which is plainly visible on a pulp filter of ordinary size, and which can be determined with exactness.

(*b*) Carried out as described below, it forms a specific, or almost specific, test for arsenic among the great majority of the commoner elements; it will be shown below, for example, that arsenic can be separated quantitatively with one precipitation from very great excess of the following metals, amongst others:—Iron, copper, lead, chromium, vanadium, manganese, nickel, cobalt, and the alkali metals, and from large excess of tin and antimony by a double precipitation. Messrs. Ridsdale's Standard "White Metal A," for which results are given below, contains small amounts of bismuth and zinc in addition to some of the above-mentioned metals, and they caused no interference. It has been shown, however, that mercury is precipitated as metal (Robinson, ANALYST, 1929, **54**, 145). Tungsten also forms an insoluble tungsten blue which masks the reaction.

(*c*) It is applicable to arsenic in either state of oxidation.

(*d*) The titration value of the precipitated arsenic as against standard iodine solution is 2·5 times the value it has in the ordinary titration.

METHOD OF DETERMINATION.—The following method was worked out for the determination of arsenic in metals, though it would, of course, be applicable to most substances, as apparently the precipitation is very immune to interference. The points to be borne in mind are the following:

(*a*) The precipitation must take place in a liquid strongly acid with hydrochloric acid; the reason for this is twofold; firstly, because the arsenic does not precipitate unless hydrochloric acid is present, and not then unless the acid concentration is somewhere about 33 per cent. of strong hydrochloric acid; secondly, because in the absence of hydrochloric acid some other metals, notably copper and bismuth, are precipitated (*cf.* Evans, ANALYST, 1922, **47**, 6).

(*b*) The liquid must be maintained, for some minutes at least, at boiling point and, as precipitation is not immediate and the solution contains a large concentration of hydrochloric acid, it is a wise precaution to carry out the precipitation under a reflux condenser.

(*c*) Strong oxidising agents should be reduced by boiling with sulphur dioxide, which must subsequently be removed by boiling. Nitric acid must be eliminated by heating with sulphuric acid until fumes appear, or may be destroyed by preliminary treatment with hypophosphite; organic matter must be destroyed by heating with sulphuric and nitric acids.

(*d*) It has been found that the reduction of certain substances, notably ferric salts, by sodium hypophosphite is apt to be somewhat slow and uncertain, tending toward low arsenic results. The addition of a little cupric sulphate seems

to catalyse this reaction, giving prompt reduction and correct results; as in other cases, possibly owing to the presence of a small amount of iron, the addition of copper has had a beneficial result, the practice has been made of always adding 0·5 grm. of copper in the form of sulphate to the liquid in each determination.

(*e*) The titration should be carried out as described in the process, for reasons which will be discussed later.

Details of the process as applied to determination of arsenic in various metals are as follows:—

COPPER.—A sample weight of 5 grms. is dissolved in a wide-mouthed beaker (without dilution) in a mixture of 20 c.c. dilute sulphuric acid (1:3) and 10 c.c. of concentrated nitric acid. When solution is complete the cover glass is removed and the liquid evaporated cautiously to dryness on the plate; this operation must be carried out on an asbestos pad, otherwise the liquid "bumps" most violently as soon as any solid separates. When the acid is fuming strongly, and the blue copper sulphate has begun to turn grey, the beaker can be placed on the naked plate and pushed gradually on to the hottest part of it; the cover glass is now replaced, tilted so as to allow escape of the acid fumes, and heating is continued until the drops of nitric acid, which at first collect on the cover-glass, are entirely evaporated. The beaker is now allowed to cool, and the copper sulphate is taken up with 75 c.c. of water; the beaker is then warmed gently until the solid is detached from the glass, and the liquid finally heated to boiling. The contents of the beaker are poured into a 750 c.c. conical flask, and the beaker rinsed in with 75 c.c. of concentrated arsenic-free hydrochloric acid. Two or 3 grms. of sodium hypophosphite are then added and the flask gently warmed until the solution is nearly colourless, if necessary a little more hypophosphite being added; the temperature should not rise above, say, 50° C. When the colour has been discharged thus, 10 grms. of hypophosphite are added, the mouth of the flask closed by a cork carrying a straight tube (approximately 60 cm. long × 1·5 cm. internal diameter) to act as a reflux condenser, the flask placed on a tripod over a burner, and its contents boiled fairly vigorously for 15 minutes (a rate of boiling such that steam issues gently from the top of the tube is suitable). The solution is next completely cooled, filtered through a pulp filter, and the precipitate washed first with 100 c.c. of dilute (1:3) hydrochloric acid to which 2 or 3 grms. of sodium hypophosphite has been added, finally, thoroughly, 6 or 7 times with 5 per cent. ammonium chloride solution. The filter is transferred to a beaker (tall form 800 c.c. capacity), and the funnel rinsed in with water, a measured excess* of standard iodine is run in from a burette, sufficient titrated water added just to cover the pulp when broken up, and the whole very thoroughly stirred and allowed to stand for about 5 minutes. (The titrated water used in this and the subsequent dilution is obtained by adding starch solution to some distilled water and titrating with $N/100$ iodine until a faint permanent

* An excess of several c.c. at least of $N/10$ or $N/100$ iodine, as the case may be, should be used. With practice, the amount required can readily be judged by the appearance of the precipitate.

blue colour appears). At the end of this time the solution is diluted to about 300 c.c. with titrated water, about 2 grms. of sodium bicarbonate added, and the solution immediately titrated with arsenious oxide solution of the same normality as the iodine used. Only an approximate end-point is obtained, and this not a complete discharge, but only a pronounced lightening of the starch blue colour; an excess of from 1 to 3 c.c. of the arsenic solution is run in, about 2 grms. more of sodium bicarbonate added, and the solution is shaken and allowed to stand until the blue colour is discharged, the liquid is finally back-titrated with iodine, the amount of the latter required being somewhere about the amount of the excess arsenic added; this final titration must be done cautiously, drop by drop, with vigorous shaking, as, if the paper pulp is once stained blue, the stain is not readily removed by the small excess of arsenic remaining; the end-point is sharp. The difference between the total volumes of iodine and arsenic solutions added gives the volume of iodine solution reduced by the precipitated arsenic.

1·0 c.c. of $N/100$ iodine = 0·00015 grm. of As.

The following results were obtained on electrolytic copper to which varying amounts of arsenic had been added.

Copper taken. Grms.	Arsenic added. c.c.	=	Grms.	Titration. c.c.		Arsenic added. Per Cent.	Arsenic found. Per Cent.
5·0	1·0	$N/100$	0·000375	2·65	$N/100$	0·0075	0·0079
5·0	2·0	$N/100$	0·00075	4·60	$N/100$	0·015	0·014
5·0	10·0	$N/100$	0·00375	2·60	$N/10$	0·075	0·078
5·0	5·0	$N/10$	0·01875	12·25	$N/10$	0·375	0·368
5·0	7·0	$N/10$	0·02625	17·20	$N/10$	0·525	0·516
5·0	7·0	$N/10$	0·02625	17·40	$N/10$	0·525	0·522

BRONZE.—It has been pointed out by S. G. Clarke (ANALYST, 1928, **53**, 377) that arsenic cannot be precipitated quantitatively from a stannic chloride solution by means of hypophosphite, owing to the precipitated arsenic reducing the tin to the stannous condition. It was found possible to eliminate this difficulty by the addition of a small amount of hydrofluoric acid; under these conditions, however, it was found that high results were obtained, due, apparently, to the co-precipitation of tin with the arsenic; consequently, the first precipitate was dissolved and re-precipitated, correct results being thus obtained.

The process is carried out exactly as described for copper up to the point where the liquid resulting from taking up the "fumed off" solid with 75 c.c. of water has been transferred to the precipitation flask and rinsed in with 75 c.c. of hydrochloric acid; 10 drops of hydrofluoric acid are then added, followed by 2 or 3 grms. of sodium hypophosphite; the flask is gently warmed until the copper has been reduced, 10 grms. more of hypophosphite are added, and the solution is boiled for 15 minutes under the reflux condenser. The liquid is cooled, filtered through a pulp filter, and washed as described for copper; the funnel is then transferred to a

clean flask, and the arsenic dissolved by treating the filter with 50 c.c. of dilute (1:1) hydrochloric acid to which a few drops of bromine have been added. The filter is washed with 100 c.c. of dilute (1:1) hydrochloric acid, 2 or 3 grms. of hypophosphite are added, and the flask gently warmed until the yellow colour of the bromine has been practically discharged; 10 grms. of hypophosphite are then added, and the arsenic re-precipitated by boiling for 15 minutes under the reflux condenser. The precipitate thus obtained is treated exactly as described for that obtained from copper.

The following results were obtained from test samples of pure copper and pure tin to which varying amounts of arsenic had been added:

Copper taken. Grms.	Tin taken. Grm.	Arsenic added. c.c.	=	Grm.	Titration. c.c.	Arsenic added. Per Cent.	Arsenic found. Per Cent.
4·95	0·05	4·0 *N*/100		0·00150	11·1 *N*/100	0·030	0·033
4·95	0·05	2·0 *N*/100		0·00075	4·6 *N*/100	0·015	0·014
4·50	0·50	2·0 *N*/100		0·00075	5·0 *N*/100	0·015	0·015
4·50	0·50	4·0 *N*/100		0·00150	8·9 *N*/100	0·030	0·027
4·50	0·50	10·0 *N*/100		0·00375	25·1 *N*/100	0·075	0·075
4·50	0·50	2·0 *N*/10		0·00750	5·2 *N*/10	0·150	0·156
4·50	0·50	4·0 *N*/10		0·01500	9·9 *N*/10	0·300	0·297
4·50	0·50	5·5 *N*/10		0·02052	13·6 *N*/10	0·411	0·408
4·50	0·50	7·0 *N*/10		0·02625	17·0 *N*/10	0·525	0·510

PLAIN CARBON STEEL.—Two points require notice with regard to the application of the method to plain carbon steels.

(*a*) As mentioned above, the reduction of ferric salts by hypophosphorous acid is apt to be slow and uncertain; the addition of a small amount of copper obviates this difficulty.

(*b*) The insoluble carbon in the sample may react with the iodine in the titration, giving high results; this difficulty is overcome by oxidation with potassium permanganate and subsequent reduction with sulphur dioxide of the manganese dioxide formed.

To a 5·0 grm. portion of the sample 0·5 grm. of electrolytic copper is added, the whole is dissolved in 30 c.c. of dilute (1:3) sulphuric acid and 15 c.c. of concentrated nitric acid, and any insoluble carbon, etc., filtered off. To the solution 30 drops of a saturated solution of potassium permanganate are added, and the liquid is boiled for five minutes; a few c.c. of a solution of sulphur dioxide are then added, and the liquid is evaporated to dryness (this may be done on the naked plate) and heated till nitric acid is completely dispelled, as described for copper. From this point forward the process described for copper is followed, except that 12 grms. of hypophosphite are used, and the preliminary warming with 2 grms. of hypophosphite is omitted.

The following results were obtained with electrolytic iron to which varying amounts of arsenic had been added:

Iron taken. Grms.	Arsenic added. c.c.	=	Grm.	Titration. Total. c.c.	Net. c.c.	Arsenic added. Per Cent.	Arsenic found. Per Cent.
5·0	Blank			0·3 *N*/100			
5·0	1·0 *N*/100		0·00037	2·5 *N*/100	2·2 *N*/100	0·0075	0·0066
5·0	3·0 *N*/100		0·00112	7·5 *N*/100	7·2 *N*/100	0·0225	0·0216
5·0	5·0 *N*/100		0·00188	12·4 *N*/100	12·1 *N*/100	0·0375	0·0363
5·0	7·0 *N*/100		0·00262	17·5 *N*/100	17·2 *N*/100	0·0525	0·0516

ALLOY STEELS.—Determinations of arsenic were made in the presence of various metals which may occur in alloy steels, the amount taken being more than the maximum likely to occur in a 5 grm. portion of an alloy steel. The determinations were carried out exactly as for 5 grms. of steel, 0·5 grms. of copper being added to each. The following results were obtained:

Metal taken.	Weight. Grms.	Arsenic added. c.c.	=	Grm.	Titration. Total. c.c.	Net. c.c.	Arsenic recovered. Grm.
Nickel	5·0	Blank			1·1 *N*/100		
,,	5·0	1·0 *N*/100		0·00037	4·5 *N*/100	3·4 *N*/100	0·00051
,,	5·0	3·0 *N*/100		0·00112	8·7 *N*/100	7·6 *N*/100	0·00114
,,	5·0	5·0 *N*/100		0·00188	13·3 *N*/100	12·2 *N*/100	0·00183
Cobalt	0·5	Blank			1·0 *N*/100		
,,	0·5	1·0 *N*/100		0·00037	3·0 *N*/100	2·0 *N*/100	0·00030
,,	0·5	3·0 *N*/100		0·00112	8·2 *N*/100	7·2 *N*/100	0·00108
,,	0·5	5·0 *N*/100		0·00188	13·2 *N*/100	12·2 *N*/100	0·00183
Chromium	1·0	Blank			0·5 *N*/100		
,,	1·0	1·0 *N*/100		0·00037	2·1 *N*/100	1·6 *N*/100	0·00025
,,	1·0	3·0 *N*/100		0·00112	6·7 *N*/100	6·2 *N*/100	0·00094
,,	1·0	5·0 *N*/100		0·00188	12·0 *N*/100	11·5 *N*/100	0·00173
Molybdenum	0·5	Blank			1·1 *N*/100		
,,	0·5	1·0 *N*/100		0·00037	2·9 *N*/100	1·8 *N*/100	0·00028
,,	0·5	3·0 *N*/100		0·00112	7·6 *N*/100	6·5 *N*/100	0·00098
,,	0·5	5·0 *N*/100		0·00188	12·1 *N*/100	11·0 *N*/100	0·00166

Trials made with tungsten by the above process broke down hopelessly, owing to the fact that the hypophosphorous acid reacts with the tungstic acid to form a dark blue insoluble compound, presumably a lower oxide, which renders any iodine titration impossible. As it was found that a large excess of phosphoric acid takes the tungstic acid into solution and apparently prevents its reduction by hypophosphorous acid, trials were made on 1·8 (=1·0 grm. of tungsten) grm. portions of sodium tungstate to which varying proportions of arsenic had been added. Each sample was dissolved in 65 c.c. of water, 10 c.c. of dilute (1:3) sulphuric acid, 0·5 grm. of copper in the form of sulphate and 20 c.c. of syrupy

phosphoric acid were added, and the liquid was warmed till it was bright; 75 c.c. of hydrochloric acid and 12 grms. of hypophosphite were then added, and the solution was boiled for 15 minutes under a reflux condenser and finished as usual. The following results were obtained:

Tungsten taken. Grms.	Arsenic added. c.c. = Grm.	Titration. Total. c.c.	Titration. Net. c.c.	Arsenic recovered. Grm.
1·0	Blank	0·5 *N*/100		
1·0	1·0 *N*/100 0·00037	2·5 *N*/100	2·0 *N*/100	0·00030
1·0	3·0 *N*/100 0·00112	6·8 *N*/100	6·3 *N*/100	0·00095
1·0	5·0 *N*/100 0·00188	12·0 *N*/100	11·5 *N*/100	0·00173

Attempts made, however, to apply this modification of the original method to steels containing high tungsten and high chromium were still unavailing, as such steels, when heated with sulphuric acid until fumes appeared, formed a pasty mass which entirely refused to go into solution again. The only alternative to the evaporation with sulphuric acid seemed to be the removal of the nitric acid by chemical means; this was ultimately accomplished by a preliminary reduction with sodium hypophosphite. The following process was worked out for tungsten steels and any that are rendered insoluble by heating with sulphuric acid until fumes appear; it can, if preferred, be applied to all steels:

A 5 grm. sample of the steel, together with 0·5 grm. of electrolytic copper, is dissolved in 30 c.c. of dilute (1:3) sulphuric acid, 15 c.c. concentrated nitric acid and 20 c.c. hydrochloric acid; 30 drops of a saturated solution of potassium permanganate are added to the liquid, which is then boiled for five minutes, after which 10 c.c. of a saturated solution of sulphur dioxide in water are added, the liquid again boiled for 2 or 3 minutes, 40 c.c. of syrupy phosphoric acid and 40 c.c. of water are added, and the liquid is boiled down to about 70 or 80 c.c. The solution is cooled, roughly measured (if less than 80 c.c. it should be made up to that volume); it is poured into a flask and an equal volume of hydrochloric acid is added and 40 c.c. of water. (This can be used to rinse in the measuring tube and beaker). About 2 grms. of sodium hypophosphite are next added, and the flask is warmed until a brisk effervescence takes place; it is then removed from the plate and sodium hypophosphite cautiously added in about 2 grm. quantities until the nitric acid is practically all dispelled, this point being indicated by the sudden cessation of the violent effervescence when more hypophosphite is dropped in. About 10 drops of hydrofluoric acid are now added, followed by 12 grms. of sodium hypophosphite; the liquid is boiled (fairly vigorously) under a reflux condenser for 15 minutes and finished as usual. In the absence of tungsten the addition of the 40 c.c. of phosphoric acid and 40 c.c. of water, also the treatment with hydrofluoric acid and the use of hydrochloric acid in the initial solution, should be omitted, and the liquid should be filtered after solution.

The following results were obtained with a synthetic mixture representing a

steel containing: Iron, 54; tungsten, 20; chromium, 20; cobalt, 5; and molybdenum, 1 per cent., to which varying amounts of arsenic had been added:

Steel taken. Grm.	Arsenic added. c.c.	= Grm.	Titration. Total. c.c.	Net. c.c.	Arsenic added. Per Cent.	Arsenic found. Per Cent.
5·0	Blank		3·4 N/100			
5·0	1·0 N/100	0·00037	5·5 N/100	2·1 N/100	0·0075	0·0063
5·0	3·0 N/100	0·00112	12·0 N/100	8·6 N/100	0·023	0·026
5·0	5·0 N/100	0·00188	16·6 N/100	13·2 N/100	0·038	0·040

BRITISH CHEMICAL STANDARD STEELS.—The arsenic in a number of British Chemical Standard steels was determined by the methods described above, the last described method being only used in the case of steel W. The following results were obtained:

Standard.	Nature of steel.	Results given on certificate. Per Cent.		Results obtained by hypophosphite process. Per Cent.
A. 2.	Mild steel	0·026 0·032	Distillation and titration with iodine.	
		0·026 0·037		0·0370
		0·036 0·023		0·0367
		0·034	As_2S_3 pptd. in distillate converted into Ag_3AsO_4 in $NaC_2H_3O_2$ solution. Dissolved in dilute HNO_3 and titrated with KCNS.	
N. 1.	Carbon steel, Mn, 0·53; Ni, 0·26	0·05 0·030 0·022 trace 0·03 0·047 0·020 0·020	Methods not given.	0·0315 0·0297
O. 1.	Carbon steel, Mn, 0·62; Ni, 0·16; Si, 0·16	0·038 0·018 0·019 0·027	Distillation and iodine titration.	0·0309 0·0312
		0·023 0·024 0·025	As_2S_3 sepn. and iodine titration.	
		0·02	Weighed as As_2S_3 and $Mg_2As_2O_7$.	

Standard.	Nature of steel.	Results given on certificate. Per Cent.		Results obtained by hypophosphite process. Per Cent.
A.	Haematite cast iron	0·040 0·042 0·045 0·041	Distillation and iodine titration.	0·0576 0·0573
		0·036	Soln. in HCl, passing evolved gas through Br water.	
		0·053	Solution in HNO_3 and reduction (*J. Iron & Steel Inst.*, 1895, i, 114).	
V.	Chrome vanadium steel, Mn, 0·54; Si, 0·16; Cr, 0·86; V, 0·27	0·016 0·015 0·016	No method given.	0·0132
B. 4.	Carbon steel, Mn, 0·73; Si, 0·03	0·138 0·138 0·142 0·145 0·140 0·140	Distillation.	0·162 0·162 0·168
W.	Chrome vanadium tungsten cobalt steel	0·01	Process not given.	0·016

These figures are of no value for the purpose of establishing the process, but they are of considerable value as a criticism of the presumably best methods available hitherto; the variation of the referee analysts among themselves (in one case (N. 1) amounting to, at least 100 per cent.) showing that all is not well with the processes used. The case of B.4 is significant. The referees' figures agree fairly closely, but the results of three closely agreeing hypophosphite determinations come 0·02 per cent. higher; examination of the figures given in this paper will show that the latter process tends to give low results rather than high. Two independent determinations by Ibbotson's method gave 0·160 and 0·167 per cent. It would seem that the distillation method may give very low results.

SIGNIFICANCE OF THE "BLANK."—The term "Blank" occurring in the various tables refers to actual arsenic in the materials (iron, nickel, etc.) used as a basis for the experiments. The reagents used appeared to be substantially free from arsenic; the arsenic was in all cases visible as a brown precipitate of about the right amount on the filter pulp; thus the term is not used in the sense of iodine adsorbed on the filter pulp or any similar gain in apparent arsenic. Some experiments made throw an interesting light on the latter question. In the process originally tried the titration was carried out in the following manner:—The filter and precipitate

were stirred with an excess of standard iodine solution, sodium bicarbonate was added, and an amount of standard arsenic exactly equivalent to the iodine added was run in; titration with standard iodine should now give an exact measure of the arsenic precipitate. For small amounts of arsenic (indeed down to quite low amounts) this was found to be the case, results of surprising accuracy being obtained; for high amounts of arsenic, however, low results were found, and the higher the amount the greater the relative loss, whilst below a certain limiting amount of arsenic results were high. It has been stated that filter pulp stirred up with iodine removes some of the iodine and that this is due to reducing substances in the pulp; suggestions have been made for preliminary treatment of the pulp with oxidising agents to remove these substances. In view of the accuracy with which small amounts of arsenic could be determined by this method, the existence of this blank seemed improbable; on determining the blank however a considerable one was found, amounting indeed to 1·0 c.c., an amount which if applied would have vitiated every one of the considerable number of accurate determinations which had been made. A blank carried out on pulp which had been treated with a solution of bromine in dilute hydrochloric acid gave substantially the same result, as also did one on asbestos pulp; it was, however, noted that the pulp always remained tinged with blue after the arsenic solution had been added, showing that iodine remained adsorbed on the pulp, although the solutions always required an excess of iodine and gave a clear end-point. A blank was therefore carried out with ordinary untreated pulp. Ten c.c. of $N/100$ iodine were added, and the mixture stirred, and 2 or 3 grms. of sodium bicarbonate were added, followed immediately by 15 c.c. of $N/100$ arsenious oxide solution; the beaker was allowed to stand for a few minutes, and the liquid was then titrated with $N/100$ iodine solution; the amount required was 5·0 c.c., the exact equivalent of the excess of arsenic added. The various results obtained are shown below:

	Excess of $N/100$ I required. c.c.
(*a*) Pulp filter stirred with 10 c.c. of $N/100$ I; back-titrated with 10 c.c. of $N/100$ As_4O_6	1·0
(*b*) Pulp treated with Br, HCl and washed; then as (*a*) ..	0·9
(*c*) Asbestos as (*a*)	0·8
(*d*) Pulp stirred with 10 c.c. of $N/100$ I; back-titrated with 15 c.c. of $N/100$ As_4O_6; re-titrated with $N/100$ I ..	no excess

The anomaly of getting accurate results on small amounts of arsenic, in spite of the existence of a relatively large blank when arsenic is not present, is therefore explained. When a certain amount of precipitated arsenic is present some of the added iodine is used up, so that the arsenic subsequently added is sufficient to extract the iodine adsorbed on the pulp; when no precipitated arsenic is present the amount of arsenic added, though sufficient to reduce the iodine, will not remove it from the pulp; hence there is in the solution an excess of arsenic which will combine with an excess of iodine. With very low amounts of arsenic the blank comes partially into operation, giving high results; with high amounts of arsenic

there is a large excess of the latter in the solution which, in its turn being adsorbed on the pulp, gives low results. The method of titration described avoids these various errors. Another source of error was found in the fact that the distilled water in use would reduce an appreciable amount of iodine; this was eliminated by adding starch to the distilled water to be used for diluting the liquid prior to titration and adding $N/100$ iodine, drop by drop, until a blue tinge appeared.

"WHITE METAL A" STANDARD.—A determination was made by the hypophosphite method of arsenic in the "White metal A" Standard of the British Chemical Standards series. The standard has the following composition:—Lead, 82·6; antimony, 12·04; tin, 4·64; copper, 0·33; iron, 0·06; bismuth, 0·03; arsenic, 0·06; zinc, 0·08 per cent.; it therefore presented certain difficulties for determination of arsenic by the usual methods, which difficulties are reflected in the diversity of the methods used by the referees. Details of the process used are as follows:—A 5 grm. sample was dissolved in a mixture of 20 c.c. of nitric acid, 100 c.c. of water, 30 c.c. of a solution of citric acid (100 grms. in 200 c.c. of water), the solution boiled and filtered, and the precipitate washed with hot water, both filtrate and precipitate being retained. The filtrate was precipitated with 20 c.c. of dilute (1:3) sulphuric acid, the precipitate filtered off and washed with 2 per cent. sulphuric acid, and the filtrate evaporated until the sulphuric acid fumed strongly, the citric acid being destroyed by repeated additions of nitric acid. The residue was taken up with 75 c.c. of water and poured into a flask, and the beaker rinsed in with 75 c.c. of hydrochloric acid; the precipitate retained from the intitial filtration was dissolved and washed through into the same flask with 100 c.c. of dilute (1:1) hydrochloric acid in repeated small quantities. To the solution in the flask 1 c.c. of hydrofluoric acid and 10 grms. of sodium hypophosphite were added; the solution was boiled for 15 minutes under a reflux condenser tube, and the precipitated arsenic, after filtering and washing as usual, was re-dissolved and re-precipitated and finished as described under bronze. The amount of arsenic thus found was 0·059 per cent.; the results of the referees' determinations, by a variety of methods, as given on the certificate were:—0·06, 0·08, 0·08, 0·04, 0·05, 0·06, 0·05, 0·05, 0·04, and 0·05 per cent.

ARSENICAL PYRITES.—Some determinations were carried out on a sample of arsenical pyrites supplied by a well-known analyst who certified the arsenical content to be 0·325 per cent.; the method used was that described for tungsten steels, omitting the use of hydrochloric acid in the initial solution and the subsequent addition of phosphoric and hydrofluoric acids. The following results were obtained:—0·339, 0·338, 0·338, 0·346 per cent.

It will be noted that the above figures, whilst being higher than that found by the donor of the sample, differ also somewhat widely amongst themselves; the sample was not very finely divided, and segregation of the arsenic is undoubtedly the explanation. Moreover, the sample was several years old, and changes may have taken place, rendering the difference from the original determination more apparent than real.

In all precipitations of arsenic with hypophosphorous acid care must be taken to keep up the concentration of hydrochloric acid; if this drops much below 33 per cent. (of the concentrated acid) the arsenic fails to precipitate, and it will be noted that the present work uniformly employs a strength of 50 per cent.; it follows from this that any washing, rinsing, etc., that may be necessary prior to precipitation and after the hydrochloric acid has been added must be done with 50 per cent. hydrochloric acid and not with water. It looks as though the reaction of arsenic salts with hypophosphorous acid involved the un-ionised trichloride and not the As''' ions.

ENGEL AND BERNARD'S METHOD.—The method published by Engel and Bernard (*loc. cit.*) is identical in principal with that advocated in this paper; they, however, introduce details, *e.g.* a digestion of 12 hours, which vastly increase the time required without increasing the accuracy; their process, too, is only concerned with the determination of arsenic, and is not worked out for its application to technical analysis.

BRANDT'S METHOD.—Brandt's process (*loc. cit.*) deals with the application of the method to ore and metal analysis. He finds that there is no loss on boiling during precipitation and does not even use a reflux condenser; this agrees with my experience; he works with a volume of 60–100 c.c. (which contains 30 to 35 c.c. of concentrated hydrochloric acid) and uses 15 grms. of hypophosphite; after adding the hypophosphite he allows the liquid to digest hot for half-an-hour and boils for 15 minutes; the present work shows the digestion to be unnecessary. With regard to titration he uses two methods (*a*) Engel and Bernard's original titration, in which an amount of iodine just sufficient to dissolve the arsenic is added, which converts the arsenic into the trivalent state, then sodium bicarbonate, finally further iodine until the starch reaction is obtained, the arsenic then being in the pentavalent state. This procedure appears to be sound though slow, but I do not agree with Brandt's suggestion that in case of over-titration (which appears to be easy) thiosulphate should be used for back-titration; a somewhat extensive comparison of this reagent with arsenious oxide showed that the latter was the better; in $N/100$ solution infinitely so. (*b*) Brandt's alternative method of titration depends on the fact that, when arsenic dissolves in iodine, acid (hydriodic and arsenic) is produced which can be used to liberate iodine from a mixture of iodide and iodate; in all, 6 atoms are liberated and 5 are reduced by the arsenic; hence As = I. This method, ingenious as it is, is completely discounted by the fact that, apart from various corrections apparently needed, 1 c.c. of standard iodine corresponds to five times the amount of arsenic that it does in either Engel and Bernard's method or in that of the present paper.

In his method for steel Brandt makes the statement that a high manganese content tends to cause the distillation method to give low results; similarly, the practice of neutralising the distillate with sodium hydroxide; this may account for the disagreements noted earlier. His method of determination of arsenic in steel seems open to criticism on one or two points: he dissolves the sample in dilute

hydrochloric acid and potassium chlorate and boils the solution down to a convenient bulk before adding the rest of the hydrochloric acid and hypophosphite; this procedure was challenged by Andrews (*Chem. Ztg.*, 1914, 295) as liable to cause loss of arsenic by volatilisation; Brandt replied that the arsenic was not lost, the concentration of hydrochloric acid being kept low. Granted that the arsenic is retained, the real explanation probably is that the arsenic is kept in the less volatile pentavalent condition; the present method renders such volatilisation impossible. As he has not added any copper Brandt relies on a rather excessive amount (40 grms. per 10 grms. of Fe) of hypophosphite for the reduction of the iron; this reduction is apt to be slow and uncertain, but the addition of a small amount of copper makes it complete and almost instantaneous. One criticism to be made of Brandt's work has to do with his plan of experimental proof; he shows that the arsenic can be separated from individual metals, he does not show that it can be separated from a complicated mixture like a modern steel; the present work shows that (*e.g.* when high chromium, high tungsten are present in a steel) this may be an unjustifiable assumption. In dealing with steel he makes no mention (*inter alia*) of tungsten; it is quite certain that his method would break down in presence of this element.

A bad feature of his method as a whole is the practice of washing the arsenic precipitate with hot water; leaving out of consideration the statement that the precipitate is easily oxidised (which Brandt denies), he frequently attempts to wash the precipitate free from a substance which is easily oxidised itself, and when oxidised is liable to attack the arsenic (*e.g.* $FeCl_2$ or Cu_2Cl_2), or from a strong reducing agent which is insoluble in hot water (*e.g.* Cu_2Cl_2) and is liable to reduce iodine. This probably accounts for his statement that copper is apt to co-precipitate with arsenic, and, moreover, prevents its complete precipitation; as shown earlier, copper exerts no deleterious action whatever. On the other hand, some of the initial work for this paper seemed to show a tendency for arsenic to dissolve slightly in water; this tendency is not uncommon in precipitated metals and was countered by the addition of ammonium chloride.

With regard to his separation from tin his results are incomprehensible. S. G. Clarke has found (*loc. cit.*) that arsenic cannot be precipitated from a hydrochloric acid solution containing a large amount of tin, and I can amply confirm that statement.

No work has been done on bismuth for this paper, but Brandt's assertion that good results can be obtained from a single precipitation, taken in conjunction with his statement that bismuth itself precipitates in weak hydrochloric acid and redissolves when more acid is added, appears dubious; every condition for co-precipitation appears to be present.

Official Appointments.

THE Minister of Health has confirmed the following appointments:—

Mr. ERIC VOELCKER, A.R.C.S.I., F.I.C., as Additional Public Analyst for the County of Buckingham (August 7, 1929) and as Additional Public Analyst for the County of Oxford (August 17, 1929).

Mr. RHYS P. CHARLES, F.I.C., as Agricultural Analyst for the County Borough of Merthyr Tydfil (August 13, 1929).

Mr. H. G. MONK, B.Sc., F.I.C., as Agricultural Analyst for the County Borough of Salford (August, 1929).

Notes.

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

OCCURRENCE OF THE TETANUS BACILLUS IN CANNED PEAS.

MANY cans in a consignment of imported canned peas were found, on arrival in this country (Persia) during the hot season, to be "blown," and the cause was made the subject of a special investigation.

The contents had a most putrid odour; the covering liquid was turbid, and particles of stalk and leaves were generously admixed with the peas.

Examination of the internal surface of a large number of cans, which were of the "sanitary" type, revealed a general and uniform dullness of the tin coating; in the vicinity of the seams there had been more intense action and the iron-plate had been exposed in a number of fine, hair-like lines. Only a trace of iron was found in the contents of each of the four cans examined chemically, but the quantity of tin which had been removed from the containers was abnormally high for this type of canned vegetable, especially so since the consignment, as far as we were able to discover, was from a recent packing. The weight of the contents of each can was approximately 400 grms., and the quantities of tin present in the peas and liquor were 0·83, 0·79, 0·74, and 1·10 grains of tin per lb., respectively.

The gas from the headspaces of four cans was collected and examined in a Bone and Wheeler apparatus, with results as below :—

Can No.	1. Per Cent.	2. Per Cent.	3. Per Cent.	4. Per Cent.
Carbon dioxide	42·3	44·0	53·6	58·2
Oxygen	0·2	0·4	Nil	0·4
Hydrogen	0·8	0·4	Nil	0·8
Nitrogen (by difference)	56·7	55·2	46·4	40·6

For the bacteriological examination two c.c. of liquor were removed from a can, with the usual aseptic precautions, one c.c. being added to each of two

Robertson's bullock's heart media tubes. This procedure was adopted for each of three other selected cans, and four tubes were incubated anaerobically at room temperature (92°–98° F.) in a Laidlaw's jar for 3 days. The remaining tubes, one from each can, were incubated at 37° C. for the same period. The results of the examination have been tabulated as follows :—

Tubes.	A.	B.	C.	D.
Aerobic. 37° C. 72 hours.	Thick reddish film on broth.	Cloudy broth. No film.	Thick reddish film on broth.	Cloudy broth. No film.
	B. subtilis *B. mycoides.* Gram-negative bacilli. No spores.	Gram-positive bacilli in chains. No spores.	Gram-negative bacilli. No spores.	Gram-positive bacilli. Mycoides type.
Anaerobic. Room temperature. 72 hours.	Deep red film on broth.	Cloudy broth. No film.	Cloudy broth. No film.	Clear broth. No film.
	B. subtilis. *B. mycoides.* Many spores.	Gram-positive bacilli in chains.	Gram-positive bacilli. Mycoides type. No spores.	Scanty gram-positive bacilli.

Anaerobic incubation was continued for a further period of four days, at the end of which time the culture in tube C showed typical *B. tetani*. A few Gram-negative bacilli were contained in the tubes A and D.

One c.c. of the broth from the tube C was injected subcutaneously into a three-quarter grown male white rat, which was examined at the end of three and four hours after inoculation. On each occasion the animal appeared to be very ill, its hind legs were partially paralysed, and its back stiffly arched. Although careful watch was made, no typical spasms were seen on these occasions. At the end of $7\frac{1}{4}$ hours the rat was found dead in a hard spasm.

Attempts were made to isolate the *B. tetani* in pure culture in order to study its immunological properties in more detail. The method of Fildes was used, but after twelve attempts it was abandoned.

Further experiments were made with ten-day anaerobic broth cultures of the mixed culture, filtered through an earthenware candle, and with the addition of a living culture of *Staphylococcus aureus*. The sterile filtrate was injected into two rats, one of which was protected with antitoxin. No ill-effects were noticeable. The strain of *tetanus* appeared to lose virulence after sub-culturing, and though both filtered and unfiltered cultures of the bacillus were injected into rats, no further evidence of toxicity was obtained.

F. MARSH.
J. HENDERSON.

ANGLO-PERSIAN OIL CO., LTD.,
PERSIAN GULF.

THE DETERMINATION OF FORMALDEHYDE IN CERTAIN PHARMACEUTICAL PREPARATIONS.

ATTEMPTS to determine formaldehyde quantitatively in a mouth-wash by the well-known methods, including the hydrogen peroxide, the iodine, and the ammonia methods, gave unsatisfactory results, probably owing to the presence of a

large number of different bodies, both organic and inorganic. A method found satisfactory was as follows:—Ten c.c. of the sample (containing about 0·2 per cent. of formaldehyde) are treated with 2 c.c. of concentrated hydrochloric acid and 10 c.c. of *N* silver nitrate solution, shaken, 4 c.c. of 30 per cent. sodium hydroxide solution immediately added, and the flask shaken again and left for 15 to 30 minutes, with occasional shaking. In the presence of formaldehyde the mixture immediately turns black. It is filtered, the precipitate washed with hot water, and the filter perforated by means of a thin stirring rod and rinsed with nitric acid (1:3) to dissolve all the reduced silver, leaving the excess of the silver chloride undissolved. After some dilution the silver chloride is filtered off, and the filtrate stirred with sufficient hydrochloric acid to precipitate the silver, which is determined in the usual manner, and converted into the corresponding amount of formaldehyde. $2AgCl = 1CH_2O$.

The following results were obtained:—

	Formaldehyde. Per Cent.
Iodine method	0·019
Hydrogen peroxide method	0·63
Silver chloride method	0·20
Actual content	0·20

The method is only applicable in the absence of sugars.

Should there be any doubt that the black precipitate is due to formaldehyde, various qualitative tests, such as the resorcinol test, may be applied to the distillate from the original preparation.

OSCAR HEIM.

244, EAST STREET 81, NEW YORK.

CORROSION-RESISTING STEEL FOR LABORATORY USE.

FOR some months past capsules of corrosion-resisting (stainless) steel have been used in this laboratory for the determination of total solids of milk and other foods.

Solutions containing fruit acids, vinegar or caustic soda of decinormal strength have no effect upon the steel, when evaporated to dryness therein on the water-bath.

A suitable size of flat-bottomed dish, somewhat similar to the porcelain milk capsule, has an outside diameter of 3 inches and is $\frac{5}{8}$ inch deep, with sloping sides and rounded corners. In gauge 24 and highly polished the weight is from 20 to 30 grms.

These dishes have the advantages over porcelain of durability and greater heat conductivity, leading to rapid drying of contents.

Their unvarying weight after continued use proves them superior to either aluminium or nickel.

The dishes at present in use have been made to the above specification in "ERA. C.R.I." Corrosion-resisting Steel by Messrs. Hadfields, Hecla Works, Sheffield, at my request.

G. A. STOKES.

ANALYTICAL LABORATORY,
179, EDGWARE ROAD, W.2.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1929.

DURING the quarter the total number of samples submitted under the Food and Drugs Act was 1275, of which 1193 were bought informally (53 adulterated) and 82 under the provisions of the Acts (20 adulterated).

BEEF SUET.—Six samples of beef suet, bought from butchers, contained 0·8 to 1·6 per cent. of moisture, 0·1 to 0·3 per cent. of ash, and up to 0·5 per cent. of fat-free membrane. All the samples contained 98 per cent. or more of fat.

Eleven samples of *shredded beef suet* contained from 0·7 to 3·5 per cent. of moisture, and from 9 to 16 per cent. of rice or wheat flour, while the fat present varied from 82 to 90 per cent. In each case the samples were marked that they were sold as mixtures, and each contained less fat than butcher's beef suet.

Five of them, however, claimed that the article was so rich in fat that 1½ lbs. equalled 2 lbs. of raw suet, and one directed that one-third less than raw suet should be used. These labels are false, as, owing to the addition of flour, beef suet contains more fat than shredded suet. In two cases similar comparisons were made with lard, and as lard is practically pure fat, this statement made the absurd claim that their article equalled 133 per cent. of fat. In each case the vendors were cautioned, and the manufacturers undertook to alter their labels.

ALLEGED LOSS OF MOISTURE IN SUGAR.—In connection with prosecutions by the Weights and Measures Department for deficiency of weight in granulated sugar that had been weighed ready for sale, the amount of moisture was determined in eight samples. Three of them lost no moisture on heating and the other 5 lost 0·01 to 0·03 per cent., disproving the suggestion of the defendant that granulated sugar was liable to lose moisture after being weighed up for sale.

PRESERVED SAUSAGE.—The three samples analysed were incorrect, as they did not contain any preservative. Vendors should make a distinction between sausage and preserved sausage.

IODINE SOLUTION.—The 1885 British Pharmacopoeia ordered a "solution of iodine" which contained 5 per cent. each of iodine and potassium iodide dissolved in water, but the article has not been contained in subsequent Pharmacopoeias. The British Pharmaceutical Codex has a "Diluted Solution of Iodine" which contains 5 per cent. of iodine and 7·5 per cent. of potassium iodide dissolved in water, and a Canadian formulary has a similar preparation.

The single informal sample examined was labelled, "Iodine Solution. Poison. Paint on the affected part with a camel hair brush." It contained only 0·8 per cent. of iodine dissolved in iso-propyl alcohol and not potassium iodide; it did not comply with any of the above standards. It barely coloured the skin when used as a paint and was probably useless. The vendor was cautioned.

SYRUP OF SQUILL.—This drug should contain at least 67 per cent. of sugar, which may become more or less changed into invert sugar. One informal sample contained only 51 per cent., and the vendor was cautioned. The other seven samples were genuine.

J. F. LIVERSEEGE.

METROPOLITAN BOROUGH OF STEPNEY.

ANNUAL REPORT OF THE BOROUGH ANALYST FOR 1928.

THE 1528 samples taken under the Food and Drugs Acts comprised 968 formal samples and 560 informal samples; 68 samples were adulterated.

GROUND GINGER.—Six of 11 samples examined were found to be adulterated with sulphur dioxide in amounts ranging from 30 to 1260 parts per million. The vendors were cautioned. Ginger may contain preservative if it is to be used in the preparation of one of the goods in which preservative is allowed (*e.g.* ginger wine), but if bought for the purpose of making cakes or puddings, it may not contain sulphur dioxide.

AMMONIATED TINCTURE OF QUININE.—A sample was found to be 15·8 per cent. deficient in ammonia. The vendor stated that he had had one pint of the tincture in stock for three days only, and that it must have been received by him at practically the same strength as that at which he had sold it. The wholesale druggists concerned made themselves responsible for the defence. The loss was attributed to evaporation of the ammonia during manufacture and while opening the bottle during dispensing, but rebutting evidence was given by the prosecution, and finally the vendor was fined £2 with £15 15s. costs (*cf.* ANALYST, 1929, 418).

CARBON DEPOSIT FROM ETHYL PETROL.—A sample obtained from the cylinder of a motor vehicle which had been running on ethyl petrol was found to contain 17·1 per cent. of lead, or 23·1 per cent. on the oil-free substance. From the total sample 2·86 grms. of metallic lead, mostly in a very finely divided state, were obtained.

DOUGLAS HENVILLE.

Legal Notes.

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

MILK CHEESE.

ON June 19 a grocer was summoned at Salford for selling cheese not of the quality demanded, and a dairy company was summoned for issuing a label which falsely described the article.

The certificate of the Public Analyst (Mr. H. H. Bagnall) stated that the cheese contained: Fat, 2·0; protein, 17·5; water, 72·5; mineral matter, 4·5; lactic acid, lactose, etc., 3·5. The following comment was made: "A genuine milk cheese should contain at least 45 per cent. of fat, calculated on a water-free cheese, whereas this sample contains 7·3 per cent. calculated in this way, and is therefore deficient of 83·3 per cent. of the minimum amount of fat."

On the label of the wrapper were the words: "The Bondon Milk Cheese. Delicious. Made by . . . Dairies."

The Inspector said that the price paid for the cheese was equivalent to 1s. 2d. per lb. In reply to the solicitor for the defence, the witness agreed that there was no standard with regard to cheese under the Food and Drugs Act, but said that there was a custom. A milk cheese should be made from milk, not from separated milk. This cheese had only about a third of the value of ordinary cheese; Cheshire cheese made from whole milk could be bought at 10d. per lb.

For the defence it was stated that the cheese was made from separated milk, with the addition of a little whole milk, and the contents were absolutely pure. The manufacturers had used the words " Milk Cheese," with the idea of avoiding any confusion with what was known as cream cheese. The wording of the label had now been altered.

The Stipendiary said that the company must take the responsibility for the shopkeeper, who would be discharged under the Probation of Offenders Act, and the company would be fined 10s. 6d. with £5 5s. costs.

ADULTERATED PEPPER. INTERMEDIATE WARRANTY.

ON June 19 a provision dealer was summoned at Tower Bridge Court for selling pepper adulterated with 50 per cent. of ground rice, and a firm of wholesale grocers was summoned for giving a false warranty.

Mr. P. Robinson, for the Bermondsey Borough Council, said that the warranty given to the retailer was not disputed, and the Council would not object to the case against him being dismissed on that ground. The Magistrate (Mr. Tassell) agreed, and the summons against the first defendant was dismissed.

There were two summonses against the wholesale firm, one under Sec. 29, for selling to the prejudice of the purchaser, and the other, under Sec. 30, for giving a false warranty. On the first summons the seller was entitled to serve notice of a warranty.

Sir R. Aske, appearing for a firm of importers, said that notice of a warranty had been served on them for selling the pepper to the wholesalers.

Mr. Robinson, continuing, said that the defendant could be discharged, provided that he proved to the satisfaction of the Court that, having bought the pepper under a warranty, he sold it as he received it, and that he had no reason at the time to believe it was otherwise than pure. If a person sold under a warranty, and that warranty proved to be false, then the onus of proof was cast upon the giver of that warranty, and the warrantor in this case had to prove that he did not rely upon the warranty received until he had taken steps to satisfy himself that it applied to the goods received.

An inspector had sampled a keg of the pepper as it was being delivered to the retailer, and had found it to be adulterated in the same way as the original sample. It was not suggested that the defendants had adulterated the pepper, but the case for the local authorities was that this firm (who had a number of local shops), when acting as wholesalers, should have convinced themselves that the article they had supplied complied with the description they had given of it.

Mr. Frampton, for the defence, said that he would prove the warranty and confine himself to the second summons, for giving a false warranty. The firm, which had been established since 1668, had placed orders for various articles with the firm of importers, and since January of this year had purchased exclusively from them their bulk of pepper, about 3 tons, of three kinds, one known as S.A.C., for which they paid 2s. 4d. per lb. They had received no complaints from anyone about the goods they had bought from this firm until the present one. They then suspended the sales of all peppers, wholesale and retail, and called in Dr. Dyer to analyse all the peppers they had in stock. His analyses showed that the only adultered pepper was the brand "S.A.C."

On every order the defendants printed the words: "Goods included in this order are to be guaranteed of the nature, substance and quality demanded." On each invoice sent by the importers was printed: "All the goods on this invoice are

warranted to be of the nature, substance and quality demanded under the Food and Drugs Act now in force, and are sold as such." He submitted that when a person bought goods under a warranty and sold them under a warranty, he was entitled to carry over to the purchaser the warranty he had received, and that he was protected as much as his own customer. In a similar case which went to the High Court (*Bell and the Dairy Supply Co.* v. *Houghton*) in 1911, it was held that where goods were bought under a warranty and sold to a customer under a warranty, that warranty held. He submitted that if he established his warranty, that was an answer to the summons for giving a false warranty.

The secretary of the defendant firm gave confirmatory evidence. He had no reason to suspect the genuineness of the pepper supplied or the truth of the warranty. In cross-examination, he admitted that they had had no analysis made until after the complaint. If they had everything analysed which they bought under a warranty, they would require an army of analysts.

The Magistrate observed that the firm seemed to have taken every reasonable, commonsense precaution from the business point of view. Under Sec. 30 a defendant was entitled to say that he had every reason to believe the description he had received under a warranty to be true, and when a reputable firm with a record like that of the defendants took every precaution, he could not believe that there was anything more to be done. Both summonses would be dismissed on the warranty.

ARTIFICIAL CREAM.

ON August 13 a "Pure Milk and Cream Company, Ltd.," was summoned at Marlborough Street Police Court for selling a substance purporting to be cream or artificial cream without having the word "cream" immediately preceded by the word "artificial" on the label, as required by the Artificial Cream Act, 1929; also for using a receptacle for the conveyance of cream without having the words "artificial cream" on it.

Mr. G. B. McClure, who appeared for the prosecutors, the National Farmers' Union, said that the Artificial Cream Act, 1929, was passed in order that a purchaser might know that he was getting artificial cream, which, in this case, could not be distinguished by analysis from ordinary cream.

Mr. B. M. Cloutman, for the defence, submitted that the National Farmers' Union was not entitled to prosecute, and that proceedings could only be taken by authorities administering the Food and Drugs Acts. The Farmers' Union had laid the information as common informers.

The Magistrate (Mr. Mead) said that the term "common informer" referred to a person who was to receive a share of the plunder. A person acting in the public interest and receiving nothing for it was in a different category.

Mr. Cloutman contended that there had only been a technical infringement of the Act. The prosecution had been brought only six weeks after the Act had been passed, while things were in a transition stage, and the fact that the food and drug authority had not seen fit to take action was a complete answer to the charge.

Mr. Mead ruled that the summons was in order. According to the Act: "It shall be the duty of every food and drug authority to enforce the provisions of this Act," but that did not prevent other people prosecuting if the food and drug authority was not sufficiently vigilant.

After evidence of the purchase and of the fact that there was no mention of artificial cream on the carton had been given, the company's sales manager gave evidence that a supply of labels and cartons complying with the Act had been

ordered immediately after the Act had been published, but that for a few days it had been necessary to use the old cartons.

In cross-examination the witness, whose attention had been called to the words on the cartons, "Specially authorised by Act of Parliament," said that he considered that the Act was passed for their benefit.

Mr. Mead, giving judgment, said that he considered the name of the company to be misleading, since an ordinary person would think that it referred to natural milk and cream. He supposed that the Act had been passed to protect the interests of farmers in this country. It might be that manufactured cream contained fewer malignant germs than natural cream, but, whether that was so or not, there was a prejudice in favour of natural cream. The price of natural cream was higher than that of the manufactured article, and therefore he thought that farmers had a right to be protected, as they were protected by the Act. Nobody could complain that, as soon as the Act was passed, the persons interested took care to see that it did not become a dead letter.

In his opinion the label was absolutely misleading. There was nothing about the cream being artificial until the label was turned round, and then the words were upside down. The label on the top had the same fault, and there was nothing on the front to show what the article was. The fact that the cream was artificial ought to be made more conspicuous. The artificiality of the cream ought not to be concealed, but should be made more prominent than anything else. In the event of another prosecution, and if this label were produced, he would probably hold that it did not comply with the Act. It was an evasion of the Act, since the public could only see that the cream was artificial by scrutinising the carton. He did not regard the offence as a technical one.

A fine of £10 2s. with £7 costs was imposed.

Mr. Cloutman asked the Magistrate to state a case on the preliminary point that he had raised, and to this Mr. Mead agreed.

"CHLORODYNE B.P. '85" WITHOUT MORPHINE.

On July 25 a firm of drug store keepers was summoned at East Ham Police Court for having sold a bottle of liquid falsely described as "Chlorodyne B.P. '85," contrary to the Merchandise Marks Act, 1887.

Mr. H. Glyn-Jones said that the Pharmaceutical Society, in accordance with its duties, had purchased, through an inspector, a bottle of liquid labelled "Chlorodyne B.P. '85." Originally the name "Chlorodyne" was that of a proprietary medicine introduced into this country about the middle of the last century, and it then contained chloroform, morphine, and dilute prussic acid. The name had since been extended to a number of similar preparations, not necessarily having the same formula, but in the British Pharmacopoeia of 1885 a specific formula was given, containing both morphine and dilute prussic acid. The defendants were in a dilemma. If they sold chlorodyne containing poison, they were committing an offence for which the Society could recover penalties. If they omitted the morphine they were committing an offence under the Merchandise Marks Act. There was an obvious danger that if the public bought an article labelled "Chlorodyne B.P. '85," they might suffer serious consequences, owing to the presence of morphine in one preparation but not in the other.

Mr. Duthie, for the defence, said that his clients had no alternative but to plead guilty. If the allegation had been that they had been selling this preparation simply as "Chlorodyne," it might have been another matter. The defendants had

actually been selling it for some time without the words "B.P. '85" on the label, but when renewing their labels they had not noticed that the new stock bore the words "Chlorodyne B.P. '85." As there was no morphine in the preparation, he asked that as lenient a view as possible might be taken.

The Stipendiary (Mr. W. W. Paine) observed that it seemed to him that, as one of the most important ingredients in the correct composition of chlorodyne was morphine, as a sedative, selling it without that was, in his opinion, a distinct fraud. He inflicted a penalty of £20, with £5 13s. 0d. for Court and special costs.

Ceylon.

REPORT OF THE GOVERNMENT ANALYST FOR 1928.

IN his annual report the Government Analyst (Mr. C. T. Symons) states that 1046 reports were made, and that 3881 articles were examined, this being a large increase on the preceding year.

MILK.—Of the 321 samples examined, only 27 were genuine; 170 of the samples contained over 25 per cent. of added water, 38 contained more than 60 per cent., and 12 contained more than 70 per cent., the maximum adulteration figure being 77 per cent. It is hoped that this appalling state of affairs does not represent a fair picture of the out-station milk supplies of the Island. There is much agitation to obtain purer water supplies, and, incidentally, this would ensure a less dangerous milk supply.

CRIMINAL INVESTIGATION WORK.—During the year there were 362 cases involving the examination of 904 exhibits. There were 78 poisoning cases (with 199 exhibits), and in 20 cases (with 39 exhibits) poison was detected. The poisons found included prussic acid (3 cases), arsenic, strychnine, acetic acid and mydriatic alkaloids (2 each), mercury, copper sulphate, croton seeds, datura seeds, hydrochloric acid, *Cerbera odollam*, kerosine oil, poisonous fish, and an unidentified poison (1 each).

Powdered glass was found in one instance, though it is doubtful whether this is to be considered an active poison if the literature on the subject is to be trusted. In this case, however, the powder also contained two teeth from a venomous snake, and some unidentified toxic substance. The intended victim noticed that the rice with which the powder was mixed had a peculiar colour, and on enquiry, was told that this was due to the rice having been boiled in a pot in which tea had been made. As the rice tasted gritty, he threw it out and washed his mouth.

Poisonous Fish.—The case of poisoning from eating some cooked fish in the Matara District is of interest. The symptoms shown by the victims were vomitting, diarrhoea and giddiness, and ended in death in a short time. The fish was apparently *Clupea moluccensis*, which is found off the Southern Coast, and is poisonous at certain seasons of the year. Some years ago there was a similar case.

Cerbera odollam.—The seeds of this plant, known locally as *veta kaduru*, contain toxic constituents. The case reported was one of suicide.

CASES OF FRAUD.—One interesting case necessitated the laborious reconstruction of a counterfeit Rs. 50 currency note from pulp chewed in a man's mouth. Apparently when this person was arrested, he at once put the note into his mouth

and chewed it up. It was forcibly removed from his mouth in a pulpy and fragmentary condition. The time spent on the work of teasing out the pulp and piecing the note together were well rewarded by the discovery that it was the work of a particular forger, whose work had appeared in the laboratory on a previous occasion.

The most interesting investigation was concerned with the alleged disappearance of most of the contents of a parcel of diamonds sent to Ceylon by registered post. The parcel, when received from the postal authorities, appeared to have all its seals intact. When opened it was evident that most of the contents had been abstracted through a hole in the tin container. Examination of the paper wrapping showed that one of the seals had been carefully cut out, leaving the tin exposed. A round hole was then made in the tin and the diamonds abstracted. Then melted sealing wax was poured on the hole and the original seal was replaced. The edges were slightly heated to make the wax of the original seal unite with the wax put on later. The whole process was most ingeniously carried out, but careful microscopical examination by ultra-violet light showed quite clearly the manner in which the fraud was carried out. Subsequent confession on the part of the culprit has shown that he did actually use the method indicated by the original examination of the packet.

THE MERCURY VAPOUR LAMP.—Some of the uses to which this lamp has been put are the following:—

(1) A seminal stain on a fabric can be localised as soon as it is seen under the lamp, and can then be removed for complete identification. This is much more rapid and certain than the old method of relying upon tactile sensation.

(2) Bleached ink writing appears clearly with almost its original darkness. This has been used many times to detect the use of stamps which have been used a second time. Such stamps, originally attached to deeds or share transfers, bore ink writing as initials and dates. This ink writing has been chemically bleached, leaving in certain cases a very passable presentation of a new unused stamp, when the process has been skilfully carried out. If one may judge by the large numbers which have been examined in these laboratories such cleaned stamps have a ready market, and many have appeared on notarial deeds, being accepted as unused stamps. Under ultra-violet light, the fraud is at once visible. In one case, which is certainly the first case in Ceylon, and possibly the first case in the East, the lamp was used in court, being connected with the electric light circuit in the Police Court, and the Police Magistrate was able to see the original writing on the stamps, which under ordinary light was quite invisible.

(3) In a case of a motor car accident from Nuwara Eliya a large number of small fragments of glass, picked up on the road and in a garage, were sent for examination to determine whether any of them, and, if so, which, corresponded with certain broken portions of the headlight lens of the car concerned. Owing to the fact that the lens glass had a peculiar fluorescence under the ultra-violet light, it was possible to pick out the corresponding pieces at once, without going to the trouble of making what would have been a very long and troublesome analysis of the glass.

(4) It was reported that certain artificial manure on a paddy field had been stolen from a particular stock. Specimens were examined under the ultra-violet lamp, and it was found that there was no resemblance between the two.

(5) The lamp has been found of great use also in the examination of counterfeit currency notes.

THE FÉRY SPECTROSCOPE.—This has been introduced for the rapid qualitative analysis of metals, and especially for tracing small impurities. By this means a photograph may be taken of the ultra-violet end of the spark spectrum of the specimen, and a comparison made with standards, or with another sample reported to be from the same source. The instrument used is only a small one, the larger pattern being very costly, and has only been in use a short time. But it is hoped that it will be of great utility in comparing, for instance, lead slugs used in shooting cases with lead found on the accused's premises, and in determining the composition of counterfeit coins without using more than a very small piece of the coin.

CHINESE CRACKERS.—No less than 69 batches of these were examined to determine whether they complied with the Customs regulations as regards import, and many were found which contained a chlorate in place of the nitrate which is alone permissible. It must be remembered that several years ago Chinese crackers were exempted from the ordinary regulations covering the import of explosives and fireworks, and could be sold without licence, since, as imported at that time, they were loaded with black powder, had little explosive power, and were thus considered to be comparatively harmless. During recent years very much larger crackers have been imported with a charge of high explosive power, consisting of aluminium powder with an oxygen carrier. These were obviously dangerous and were prohibited, but after this the manufacturers, presumably in order to provide a cracker with more explosive power than the old black powder one, used potassium chlorate in place of the nitrate, and again contravened the regulations.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Evaluation of Crab Preparations and Detection of Crab Ingredients. G. Büttner and A. Miermeister. (*Z. Unters. Lebensm.*, 1929, **57**, 431–437.)—Genuine crab preparations contain three natural colouring matters—the green or blue "cyanocrystallin," the red "crustaceorubin," and the yellow "crustaceofulvin," all of which are lipochromes and are soluble in oils and in organic solvents, but not in hot or cold water, acids or alkalis. Cooking transforms the first into the second-named colour, so that red predominates. Concentrated sulphuric acid or alkaline potassium iodide solution produces a blue-green colour, but no characteristic luminescence is produced in ultra-violet light, though the uncoloured portion (flesh and muscle) of the crab gives a pale blue light. Dyes used to imitate crab colour (Orange I, II, G and GG, Tropaeolin and Tropaeolin 000) are usually soluble in water, fat, and alcohol, and may be detected by the fact that they are rapidly destroyed by reduction with zinc and hydrochloric acid, but not with nitrites or sulphites, whilst the natural colour is stable. For the test 20 grms. of sample are ground in a mortar with sand, and heated under a reflux condenser with 150 c.c. of 96 per cent. alcohol for 3 hours. The fat is separated from the filtered liquid by cooling it in ice-water for 2 hours, the liquid re-filtered, evaporated

to 10 c.c., cooled and again filtered. The filtrate is shaken with 2 c.c. of zinc chloride solution and 2 c.c. of hydrochloric acid; if the solution is colourless after 1 hour, no natural colour is present. Yellow to red colours indicate increasingly large proportions of natural colour. Wool tests will not distinguish natural and artificial colours. Ultra-violet light destroys the genuine colour completely, and daylight destroys it partly, but the colour is stable in the dark. A 0·1 *N* solution of sodium dichromate was used as colour standard for these tests.

J. G.

Normal Occurrence of Arsenic in Fish and in Cod-liver Oil. E. Sadolin. (*Dansk. Tids. Farm.*, 1928, **2** (7), 186; *Chem. Abs.*, 1929, **23**, 210.)—Two samples of codfish flesh gave, respectively, 0·4 and 0·8 mgrm. of arsenic per kilo; cod-liver, 0·7 and 3·2 mgrm.; and for cod-liver oil, 3·0 to 4·5 mgrm. was the normal figure. Eel oil, extracted by ether, contained 0·6 mgrm. of arsenic per kilo., herrings (muscular tissue) 2 mgrms. per kilo., and (oil) 9 mgrms., per kilo. D. G. H.

Seed Fats of some Cultivated Species of Umbelliferae. B. C. Christian and T. P. Hilditch. (*Biochem. J.*, **23**, 327–338.)—The percentage compositions of the fatty acids obtained from certain fats were:

	Palmitic acid.	Petroselinic acid.	Oleic acid.	Linolic acid.
Fennel	4	60	22	14
Carrot	4	58	14	24
Coriander	8	53	32	7
Celery	3	51	26	20
Parsnip	1	46	32	21
Chervil	5	41	0·5	53·5
Caraway	3	26	40	31

The view that petroselenic acid (Δ6:7-octadecenoic acid) is characteristic of umbellate seed fats is strengthened. In all cases considerable amounts of resinous and unsaponifiable matters were present; this makes the quantitative results somewhat less certain than in their absence. An attempt to determine whether the composition of the endosperm fat differed from that of the fatty oil was inconclusive. D. G. H.

Quantitative Examination of the Kreis Rancidity Reaction. J. Pritzker and R. Jungkunz. (*Z. Unters. Lebensm.*, 1929, **57**, 419–421.)—One drop (0·5 mgrm.) of a fresh aqueous 1 per cent. solution of acrolein are mixed with 3 drops of 3 per cent. hydrogen peroxide solution in a stoppered cylinder, and after 3 hours in darkness 5 c.c. of concentrated hydrochloric acid (sp. gr. 1·19) are added, and the mixture shaken for 1 minute. After the addition of 5 c.c. of a 1 per cent. solution of phloroglucinol in ether a bright red colour is obtained which reaches a maximum after 5 minutes, and, if produced from 0·5 mgrm. of acrolein, may be matched in shade by 1·2 mgrms. of potassium permanganate in 100 c.c. of water (or 3·8 c.c. of 0·01 *N* solution). In this version of the Kreis test the acrolein is completely oxidised by the hydrogen peroxide to epihydrinaldehyde,

the sensitiveness of the test being 1:100,000, and the upper detectable limit 10 mgrms. of aldehyde in 100 c.c. of oil. The method has been compared with that of von Fellenberg (ANALYST, 1925, **50**, 245), and 10-year old samples of olive, soya and maize oils, arachis oil (2 years), lard (1 year) and butter fat (14 years) were found to contain 60, 60, 20, 100, 200, and 400 mgrms. of epihydrinaldehyde per 100 grms., respectively. Since, in the extreme case, the proportion of decomposed fat corresponds with about 13 times the amount of aldehyde found, these samples were decomposed to the extent of 0·3 to 5 per cent. (*cf.* ANALYST, 1926, **51**, 635; 1929, 411). J. G.

Detection of Rancidity in Fats from intact Seeds and Fruits. A. Niethammer. (*Z. Unters. Lebensm.*, 1929, **57**, 358–360.)—The sample is well disintegrated in a dish, placed in a linen bag previously extracted in succession with acetone and chloroform and washed with distilled water, and extracted with petroleum spirit under a reflux condenser. The solvent is distilled from the extract, and the Kreis and Fellenberg tests applied (Pritzker and Jungkunz, ANALYST, 1926, **51**, 635). Old samples of *Zea mays*, *Linum usitatissimum*, *Cannabis sativa*, *Helianthus annuus*, and *Papaver somniferum* gave positive results, but fresh samples gave no reaction. J. G.

Fatty Acids Associated with Rice Starch. L. Lehrman. (*J. Amer. Chem. Soc.*, 1929, **51**, 2185–2188.)—An investigation of the fatty acids associated with rice starch (α-amylose portion) disclosed the presence of 36 per cent. of palmitic acid, 35 per cent. of oleic, and 29 per cent. of linolic acid. There were probably no other substances in the fatty acid mixture obtained by extracting the solid material resulting from the hydrolysis of rice starch. D. G. H.

Petroleum Spirit Test for Purity of Castor Oil. T. Cocking. (*Pharm. J.*, 1929, **123**, 11.)—The limits of the Pharmacopoeia petroleum spirit solubility test are considered too wide to justify its retention. Pure castor oil was found not to pass the test unless some aromatic hydrocarbon was present in the spirit. With pure hexane as solvent the clearing points showed a divergence of as much as 9·5° for different genuine oils, and a clearing point of 22·3° C. given by one genuine oil corresponded with that given by another genuine oil to which 9 per cent. of olive oil had been added. D. G. H.

New Reaction for the Identification of Urotropine in Wines. M. V. Ionescu and C. Bodea. (*Bull. Soc. Chim.*, 1929, **45**, 466–468.)—The following reaction serves for the detection of urotropine or formaldehyde in sulphited or non-sulphited wines. The clear wine (2 to 5 c.c.) is treated with 1 to 2 volumes of 0·7 per cent. aqueous dimethyl-dihydro-resorcinol solution. The separation of a white crystalline precipitate of methylene-bisdimethyl-dihydroresorcinol, with m.pt. 184–187° C., after about 15 minutes, or sooner if the liquid is boiled, indicates either formaldehyde or urotropine. The reaction is given by 0·02 grm. of urotropine, or the corresponding amount of formaldehyde, per litre of wine.

T. H. P.

Chemical Constitution of the Gums. Part I. Nature of Gum Arabic and the Biochemical Classification of the Gums. A. G. Norman. (*Biochem. J.*, 1929, **23**, 524–535.)—A detailed examination of acid gum arabic showed the acid group to be of the uronic type, and the only two sugars present to be galactose and arabinose. The acid hydrolysis products were obtained by boiling the gum with 3 per cent. sulphuric acid for a definite period, and, while still very hot, neutralising the acid by finely divided barium carbonate, and, after a few moments, filtering off the precipitate. Boiling alcohol is poured into the hot filtrate until the alcohol concentration reaches 60 per cent., when the precipitate settles quickly, and the supernatant liquid is at once poured off. The end product is thus free from galactose and arabinose. The precipitate is dissolved in water, the solution filtered, heated nearly to boiling, and reprecipitated, and this process is repeated several times. Analyses of the original product after 1, 3 and 5 hours' hydrolysis were made, and it is concluded that gum arabic has no definite empyrical formula, but probably consists of a nucleus acid made up of galactose and a uronic acid, probably galacturonic acid, to which is linked arabinose by glucosidic linkages, so that the arabinose is more easily split off than the other components. The structural resemblance to hemicellulose is close, and it is suggested that protracted mild oxidation of linked hexose, and particularly galactose units, results in the formation of pectin, hemicelluloses and gums. The analysis of one sample of acid gum arabic gave the following results:—Ash, 0·24; furfuraldehyde yield (ash-free), 13·93; carbon dioxide yield (ash-free), 4·39; uronic acid anhydride, 17·56; furfuraldehyde due to uronic acid, 2·91; anhydroarabinose, 20·52; and anhydrogalactose (yielding arabinose 23·52, and galactose 68·80 per cent.), 61·92 per cent. D. G. H.

Determination of Pyrethrin I and II in Pyrethrum. F. Tattersfield and R. P. Hobson. (*J. Agric. Sci.*, 1929, **19**, 433–437.)—As the acid method of determining pyrethrin I and II (ANALYST, 1929, 351) requires several days for its completion, the following rapid method has been devised for the evaluation of pyrethrum by determining pyrethrin I, which is the more important of the two poisons present. Ten grms. of the ground pyrethrum are extracted in a Soxhlet apparatus with petroleum spirit (b.pt. 40° to 50° C.), which is kept vigorously boiling over a carbon-filament lamp. When the solvent draining over is colourless, the petroleum spirit solution, which should have a volume of about 50 c.c., is placed in a long-necked 100 c.c. flask to be used for the subsequent distillation, the extraction flask being rinsed once with a iittle petroleum spirit. After addition of 4 to 5 c.c. of *N*-sodium hydroxide (in methyl alcohol), the mixture is boiled under a reflux condenser on a water-bath for 1½–2 hours. The liquid is acidified with *N*-sulphuric acid and steam-distilled. When 50 c.c. of aqueous distillate have collected below the petroleum spirit the receiver is changed, and a further 50 c.c. are collected. The first distillate is vigorously shaken for a minute in a fairly large separating funnel, the aqueous layer being separated and the petroleum layer washed once with water and run into a flask containing 20 c.c. of water, a few

drops of alcohol, phenolphthalein, and just enough alkali to give a faint pink colour. Titration with $N/50$ soda is carried on until the aqueous layer is distinctly alkaline after vigorous shaking in the corked flask. The second 50 c.c. of distillate are added to the first aqueous fraction (already extracted once), and the whole vigorously shaken with 50 c.c. of petroleum spirit, the washed petroleum layer being added to the titration flask, and the titration finished as before; very little additional alkali is usually needed. After deduction from the titration reading of a blank determined for the petroleum spirit (about 0·2 c.c. of $N/50$ soda), the monocarboxylic acid and pyrethrin I contents may be calculated: 1 c.c. $N/50$ alkali = 3·36 mgrms. monocarboxylic acid = 6·6 mgrms. pyrethrin I. T. H. P.

Determination of Ammonia and Amide Nitrogen in Tobacco by the Use of Permutit. H. B. Vickery and G. W. Pucher. (*J. Biol. Chem.*, 1929, **83**, 1–10.)—The accurate determination of the pre-existing ammonia or of the amide nitrogen of tobacco is rendered difficult by the volatility of nicotine which distils over more or less completely when the standard procedures for the determination of these forms of nitrogen are used; no satisfactory correction method for the nicotine content of such distillates has yet been found. During an investigation of the tobacco leaf it became necessary to determine accurately the simpler forms of nitrogen in the green leaf as well as in manufactured tobacco, and a method which was devised for the determination of pre-formed ammonia and of amide nitrogen in the tobacco is now described. The ammonia is distilled from the untreated or hydrolysed sample into acid, according to the technique of Folin and Wright (*J. Biol. Chem.*, 1919, **38**, 461), then, as described by Folin and Bell (*J. Biol. Chem.*, 1917, **29**, 329), removed by permutit, liberated subsequently from the permutit by alkali, and determined colorimetrically by the use of Nessler's reagent. The nicotine does not interfere; it is absorbed by permutit only to a very small extent, and gives no appreciable colour with Nessler's reagent. The base exchange relationships of monomethyl-, dimethyl- and trimethylamine with permutit were also studied; none of these amines interferes with the determination of ammonia, although data by Whitehorn (*J. Biol. Chem.*, 1923, **56**, 751; ANALYST, 1923, **48**, 565) indicated that nicotine and several of the volatile amines undergo extensive base exchange with permutit. The new method is simple and rapid and can readily be employed in the investigation of other tissues. Ammonia added to tobacco extracts can be recovered with an average accuracy of 95 per cent. Amide nitrogen of asparagine added can be recovered with an average accuracy of 92·5 per cent.; this lower result is to be expected, as the proportion of amide nitrogen is calculated from the difference in ammonia content before and after hydrolysis, and therefore contains the error of the ammonia determination twice over. P. H. P.

Caffeine-Salicylic Acid a Molecular Compound. N. Schoorl. (*Pharm. Weekblad*, 1929, **66**, 357–358.)—The solubility of caffeine in water (2 per cent.) is increased if the caffeine is combined with salicylic acid (ANALYST, 1924, **49**, 486), and the air-dried commercial sodium salt, $C_8H_{10}N_4O_2$, $C_7H_5O_3Na$, $5H_2O$, prepared

by crystallisation from warm water of an equimolecular mixture of sodium salicylate and caffeine ($C_8H_{10}N_4O_2$, $5/6H_2O$) contains 20·2 per cent. of water of crystallisation. It is pointed out that the whole of the water of crystallisation is removed after 1 day in a desiccator, and the requirements of the Dutch Pharmacopoeias are criticised from this point of view. J. G.

Salicyl-sulphonic Acid. J. Rae. (*Pharm. J.*, 1929, **122**, 618.)—Seven samples of salicyl-sulphonic acid were examined for colour and moisture percentage, purity (by titration with 0·1 *N* sodium hydroxide), sulphate (by the U.S.P. turbidity method), free salicylic acid, and m.pt. The results showed that two salts are on the market, one with a m.pt. of about 110° C. and the other of 120–124° C. The other results, although varying somewhat, did not fall into coinciding groups. D. G. H.

Quantitative Determination of Methylene Blue. M. François and L. Sequin. (*J. Pharm. Chim.*, 1929, (8), **10**, 5–9.)—Owing to the increasing use of methylene blue in therapeutics the authors have devised a method for its quantitative determination. The principle of the method is based on the fact that methylene blue, which behaves analytically like an alkaloid, is completely precipitated by a solution of picric acid. A volumetric method was first tried, but, as titration with picric acid did not give a definite end-point, this was rejected in favour of a gravimetric method, the technique of which is as follows:—One grm. of methylene blue is weighed out carefully, and placed in a small conical flask. In order to obtain complete solution water is added in portions of 10 c.c., each portion is poured through a funnel, containing a small plug of cotton, into a 100 c.c. flask, the flask and funnel are washed, the contents made up to 100 c.c., and the flask shaken. Ten c.c. of this solution (which contain 0·1 grm. of methylene blue) are placed in a 125 c.c. conical flask, and 20 c.c. of an aqueous solution (5 grms. per litre) of picric acid are added. Immediately a purple-black precipitate is formed and leaves a clear yellow solution. After filtration the precipitate is carefully washed with 10 c.c. of water to remove any excess of picric acid, pressed lightly between filter papers, then left to dry (either in the air or in a desiccator over sulphuric acid), and weighed. The crystalline picrate which is precipitated is formed of one molecule of methylene blue and one molecule of picric acid with no water of crystallisation. The molecular weight of picric acid is 229, that of methylene blue 373·5 (with 3 molecules of water), or 319·5 (anhydrous); thus the molecular weight of the picrate is 548·5. Therefore to obtain the weight of methylene blue, the weight of the dry precipitate is multiplied by $\frac{373{\cdot}5}{548{\cdot}5}$, or 0·6809. Analyses of pure samples which have been carried out show very satisfactory results with this method. When solutions have to be analysed, amounts which contain approximately 0·1 grm. of methylene blue should be taken. If other compounds are likely to be present, care must be taken to eliminate first of all the substances which may be precipitated by picric acid, such as alkaloids, albuminoids and ammonium and potassium salts. P. H. P.

Detection of Isopropyl Alcohol in Cosmetics by Means of Piperonal. G. Reif. (*Z. Unters. Lebensm.*, 1929, **57**, 277–288.)—The author's method (ANALYST, 1928, **53**, 497) is modified as follows:—The alcohol is removed from 10 c.c. of the sample by distillation on the water-bath, and collected in a receiver cooled in ice-water. To 1 c.c. of the distillate are added 3 c.c. of hydroxylamine hydrochloride solution containing 0·05 grm. for mouth-washes or scents and 0·1 grm. for hair-washes (which may contain tincture of cantharides). The mixture is well shaken, allowed to stand for 3 minutes at room temperature, 0·4 grm. of medicinal carbon (*Carbo medicinalis*) added, and the whole well shaken. After filtration through a dry paper into a 100 c.c. boiling flask, the clear liquid is mixed with 5 c.c. of a 0·5 per cent. solution of piperonal in absolute alcohol, and 20 c.c. of concentrated sulphuric acid (sp. gr. 1·84) added carefully, to avoid boiling. Five c.c. of the mixture are then heated on the water-bath for 5 minutes. In the absence of isopropyl alcohol a brown or green-brown colour appears, or in its presence a red or red-brown colour. If 30 c.c. of a 30 per cent. solution of acetic acid are at once added a greyish-yellow or transitory red colour is obtained in the absence of the alcohol, or a red-brown colour, turning red after 10 minutes, appears in its presence. The method was tested for a number of cosmetics of known and varied compositions, and shown to be independent of the presence of fusel oil, denaturants or other constituents. J. G.

Tin-Foil as a Packing for Rindless Cheese. Elten. (*Chem. Ztg.*, 1929, **53**, 586.)—The foils examined contained 96 to 98 per cent. of tin, 2 to 4 per cent. of antimony, 0·1 to 0·2 per cent. of lead and traces of copper and iron, and were discoloured in places. The portions of the cheese in contact with the darkened portions contained 2·1 to 2·3 per cent. of tin, and had an acid of 2·4 to 2·6, whilst the acidity of the remainder was 1·6. The importance of the use of a good valve-quality product of low acid content, particularly when the melted cheese is allowed to set in its tinfoil container, is emphasised. J. G.

Lead in Red Glaze. A. Gronover and E. Wohnlich. (*Z. Unters. Lebensm.*, 1929, **57**, 360–363.)—The red glaze or enamel of certain culinary ware may contain lead chromate, and the conditions of extraction of the lead for the purposes of analysis are discussed. It is recommended that the glaze be well scalded with hot water, two-thirds filled with 4 per cent. vinegar, and heated on the water-bath for 30 minutes. Ten successive treatments of this type removed approximately the same amount of lead (about 7 mgrms.) for each extraction. The lead was determined by Sudenorf and Penndorf's modification of Winkler's colorimetric method (*id.*, 1923, **45**, 361), and by the volumetric chromate method. After extraction a white, water-soluble efflorescence containing carbonate, sulphate, acetate and aluminium, was observed on the enamel. J. G.

Biochemical.

Improved Colorimetric Method for the Determination of Cystine in Proteins. O. Folin and A. D. Marenzi. (*J. Biol. Chem.*, 1929, **83**, 103–108.)—The validity of the method of Folin and Looney (*J. Biol. Chem.*, 1922, **51**, 427; ANALYST, 1922, **47**, 359) for the determination of cystine in protein hydrolysates has been re-examined. The method has been criticised at different times, and accurate cystine determinations have become increasingly important. The Folin-Looney method as it stands in the literature has two known defects. It does not provide for the removal of molybdate (and phenol reagent) from the uric acid reagent, and thus it is possible that some tyrosine is included in the cystine determinations; for the same reason, the reagent gives an uncomfortably large blank with the sodium sulphite used for the preliminary reduction of cystine to cysteine. A third defect, discovered in the course of the work, is that cysteine reacts less rapidly with the uric acid reagent than does uric acid. To obtain complete reaction with the cysteine necessitates the addition of much more of the uric acid reagent than was originally used. A uric acid reagent entirely free from phenol reagent has now been prepared by the authors (*J. Biol. Chem.*, 1929, **83**, 109–113), and with this phosphotungstic acid reagent the influence of tyrosine is entirely eliminated, and also the third defect is remedied. By the addition of the sulphite to the acid cystine solution, that is, before instead of after the carbonate, the amount of 20 per cent. sulphite used is reduced from 10 c.c. to 2 c.c., and thus the blank produced by the sulphite becomes negligible. On the basis of these improvements it has been found possible to obtain a true range of proportionality between colours obtained from different amounts of cystine between 10 mm. and 40 mm. when the standard is set at 20 mm. The blue solutions are diluted with 3 per cent. sodium sulphite solutions instead of water to avoid a bleaching effect. The sum total of all these refinements of the Folin-Looney method for the determination of cystine is so great that there can scarcely be any comparison in the dependability of the results obtained by the two forms of the method. The method is described in detail. Samples of casein, gliadin, edestin, zein, egg albumin and serum albumin have been examined for their cystine content; the results given obtained by the new method are higher than the figures obtained by the original method except in the case of gliadin, the figures for which are slightly lower. P. H. P.

Determination of Carbon Monoxide in Blood. W. M. M. Pilaar. (*J. Biol. Chem.*, 1929, **83**, 43–50.)—Most of the known methods for the quantitative determination of carbon monoxide in blood are briefly discussed and criticised. The method of Cohen Tervaert (*Biochem. J.*, 1925, **19**, 300) has now been modified and converted into a micro method. In the original method the carbon monoxide is liberated by the addition of potassium ferricyanide in a vacuum. It then reacts with iodine pentoxide, heated to 150° C., according to the reaction— $I_2O_5 + 5CO \rightarrow 5CO_2 + I_2$, and the iodine liberated is absorbed in a potassium iodide solution and titrated with 0·01 *N* thiosulphate solution from a micro burette.

This procedure is subject to the following criticisms: (1) The amount of blood necessary for a determination is 10 c.c., and necessitates venepuncture, (2) the large Peligot tubes of the apparatus seem unsuitable, especially for taking up the iodine, (3) some of the iodine is absorbed by the rubber stoppers and tubing, and (4) the concentration of the potassium iodide solution recommended (0·5 per cent.) is too low, and results in low figures in cases of high carbon monoxide content. The modified apparatus for the new method is shown in a figure and described, and details of the method are given. Only 1 c.c. of blood, which can be obtained from a finger tip or ear lobe, is necessary for a determination. Tables show the recovery of carbon monoxide from air and from blood by this method. The method is being applied to the examination of blood from people who, as a result of their occupation, are exposed to carbon monoxide. Motor car drivers and garage workers are the chief cases. Some of the results obtained are given. It is stated that 1 c.c. of blood from an adult with an average haemoglobin content can contain a maximum of about 0·250 c.c. of carbon monoxide. Whenever 20 to 30 per cent. of this is present, rather serious acute symptoms can be found. P. H. P.

Quantitative Determination of Bile Acids by means of a New Colour Reaction and Monochromatic Light. R. Gregory and T. A. Pascoe. (*J. Biol. Chem.*, 1929, **83**, 35–42.)—The Pettenkofer reaction (*Ann. Chem.*, 1844, **52**, 90) was studied and found unsuitable for the quantitative determination of bile acids in pure solutions, and unreliable for even qualitative work on body fluids. A new colour reaction for the determination of bile acids is described which is more specific and more accurate than the Pettenkofer procedure. When to a dilute bile acid solution are added 34 per cent. of sulphuric acid by volume and 0·05 per cent. of furfural by volume, and the mixture is heated for 30 minutes at 65° C., a pure blue colour results, which is different from any that has been reported in the literature. The blue-coloured compound is stable for 2 to 3 hours, perfectly reproducible, and quantitative in character; *i.e.*, it conforms to Beer's law. The reaction which gives the blue colour is called the Gregory reaction. Portions of sodium glycocholate solutions of known concentration (0·1 and 0·2 mgrms. per c.c.) were measured into test-tubes with a calibrated micro burette, made up to 1 c.c. with distilled water, 6 c.c. of 45 per cent. sulphuric acid solution were added, then 1 c.c. of 0·3 per cent. furfural solution, and the tubes were loosely stoppered and set in a water-bath at 65° C. for 30 minutes, and then compared with a standard solution. Very good results were obtained, but in all cases when the concentration was less than that of the standard there was a positive error, whilst a greater concentration than the standard always gave a negative error. Various substances other than bile acids that give a positive Pettenkofer reaction, including glycine, taurine, cholesterol, lanolin, lecithin, cephalin and oleic acid, gave negative results when tested in this way. Since these include the substances that might be present in blood, and as an alcoholic extract of normal blood does not give the Gregory reaction, the test is suitable for the determination of bile acids in an alcoholic extract of blood. In the presence

of bile pigments simple colorimetric analysis failed, and a spectrophotometric study of the blue colour of the Gregory reaction was therefore made. A marked absorption band was shown, the centre of which was at 6200 Å. A new, simple and inexpensive apparatus for obtaining monochromatic light of this wave-length (about 6200 Å) for illumination of the colorimeter was devised for use in the study of the bile acid content of bile and blood. Results show that by means of the new colour reaction and monochromatic light it is possible to determine bile salts in bile quantitatively, which is not possible with the Pettenkofer reaction. In no instance did the presence of the relatively large amounts of bile pigment interfere with the comparison of the colour in the bile solutions with that of standards prepared from pure sodium glycocholate. No bile salts were found in two trials with about 5 litres each of normal ox-blood. These results are contrary to those of Roundtree, Greene and Aldrich (*J. Clin. Inv.*, 1927, **4**, 545), who reported the presence of 2·5 to 6 mgrms. of bile salts per 100 c.c. of normal human blood. Bile acids or their salts are insoluble in ordinary fat solvents, but readily soluble in the solution of fat in these solvents. P. H. P.

Distribution of Copper in Blood. C. A. Elvehjem, H. Steenbock and E. B. Hart. (*J. Biol. Chem.*, 1929, **83**, 21–25.)—Some samples of haemoglobin have been analysed for copper; no studies have previously been made directly on this pigment, and the possibility of the presence of copper in the molecule is the first question to be answered in the determination of the function of copper in haemoglobin building. Two samples of horse blood gave 0·034 mgrm. of copper and 0·019 mgrm. of copper per grm. of dry haemoglobin respectively; thus on the assumption that there is 1 atom of copper per molecule of haemoglobin, the smallest calculated molecular weights are 1,870,588 and 3,344,368 respectively, both of which are many times the accepted value. The sample purified to the largest extent contained the smallest amount of copper. The original work showing the importance of copper as a supplement to iron for haemoglobin building was conducted with rats, and therefore similar analyses have also been carried out on haemoglobin from rat blood, prepared according to the method of Heidelberger (*J. Biol. Chem.*, 1922, **53**, 31). An average of 0·015 mgrm. of copper per grm. of oxyhaemoglobin was obtained, from which the calculated molecular weight is 4,240,000. Therefore, if the molecular weight of haemoglobin is accepted as 16,700 (the early figure) or 66,800, as recently reported by Svedberg and Fahraeus (*J. Amer. Chem. Soc.*, 1926, **48**, 430), then the haemoglobin of rat blood does not contain copper as part of its molecule. The copper content of horse blood has been determined and found to be approximately 0·05 mgrm. of copper per 100 c.c. of blood. The corpuscle fraction of blood, whether prepared by centrifuging oxalated blood, or defibrinated blood, contains the largest portion of the copper. Further work must be done to establish the exact relation of these minute traces of copper and the blood. P. H. P.

Effect of Diet on the Copper Content of Milk. C. A. Elvehjem, H. Steenbock and E. B. Hart. (*J. Biol. Chem.*, 1929, **83**, 27–34.)—A recent publication by Hart, Steenbock, Waddell and Elvehjem (*J. Biol. Chem.*, 1928, **77**,

797) demonstrated the importance of copper as a supplement to iron in the prevention of anaemia in rats kept on a diet of whole cow's milk. Experiments have now been carried out to determine the actual amount of copper present in cow's milk, to detect variations in the copper content which might appear in milk produced under different conditions, and to show whether the copper content of cow's milk can be increased appreciably by the addition of copper salts to the normal ration of a cow. Different workers have reported wide variations in the time required for rats to become anaemic on a whole milk diet; it was hoped by this work to show whether the copper content of milk can be varied enough to account for these differences. Analyses are presented of samples of milk from individual cows and goats which have been fed on a normal ration or one supplemented with copper, and the analyses of composite samples of milk obtained from herds of cows located in various sections of the United States. The results show that milk produced by cows on a normal ration contains about 0·15 mgrm. of copper per litre. This figure is considerably lower than most figures for raw milk reported in the literature. The authors believe that many of the high figures reported are due to copper contamination during the process of analysis, especially from the dishes used for the ignition of the milk. The copper content of cow's milk cannot be increased by feeding the cows with sufficient copper sulphate to increase the copper intake 5-fold. Samples of cow's milk collected from thirteen herds located in different states showed very slight differences in copper content. The figures ranged from 0·123 mgrm. per litre for the milk from North Carolina to 0·184 mgrm. per litre for the milk from Texas. The copper content of goat milk was not increased when the copper content of the ration was increased five to ten-fold. Further, limited numbers of analyses for copper did not indicate a decidedly lower amount of this element in goat milk as compared with cow's milk; this is contrary to the results of Quam and Hellwig (*J. Biol. Chem.*, 1928, **78**, 681; ANALYST, 1928, **53**, 542). It is concluded that the difference in the rate of anaemia production in rats on whole milk diets, reported by different investigators, cannot be due to a variation in the copper content of the milk when produced, but rather to the contamination of the milk after production, or to unknown sources of copper supply during the different periods of the rat's life. P. H. P.

Iron in Nutrition. IX. Further Proof that the Anaemia Produced on Diets of Whole Milk and Iron is due to a Deficiency of Copper. J. Waddell, H. Steenbock, C. A. Elvehjem and E. B. Hart. (*J. Biol. Chem.*, 1929, **83**, 251–260.)—It was shown recently by the authors (*J. Biol. Chem.*, 1928, **77**, 777, 797) that copper in varying amounts was present in all their fractions which cured the anaemia developed in rats on a diet of cow's whole milk and iron. However, the question arose as to whether or not copper was the only element occurring in the preparations which could supplement iron in the cure and prevention of the particular type of anaemia being studied, and results are now presented of experiments which have been carried out, and which show the specificity of copper in this respect. The authors used a variety of preparations, and compared them

all on the basis of their copper content, so that any other substance (or substances), *organic* or *inorganic* in nature, that was potent in haemoglobin regeneration would reveal its presence, especially when the copper intake was very low. Several liver preparations, hydrogen sulphide fractions of the acid extracts of the ashes of two of them, and copper as a solution of copper sulphate, all on the same levels of copper intake, were shown to serve equally well as supplements of a basal diet of whole milk and iron, to cure the nutritional anaemia produced by the basal diet. This is, therefore, additional and convincing proof that the deficiency of this basal diet is *inorganic* in nature, and that this inorganic deficiency is copper only.

P. H. P.

Effect of Heat on Milk. (a) On the Coagulability by Rennet, and (b) On the Nitrogen, Phosphorus, and Calcium Contents. E. C. V. Mattick and H. S. Hallett. (*J. Agric. Sci.*, 1929, **19**, 452–462.)—Since the addition of a solution of a calcium salt to pasteurised milk permits of the formation of an almost normal curd by the action of rennet, it appears that the heating affects mainly the calcium salts of the milk. The experiments now described show that milk which has been heated for 30 minutes to temperatures ranging from 105° to 209° F. differs from raw milk in its reaction towards rennet in all cases. No change is observed in the diffusibility of the nitrogenous substances of the milk as a result of such treatment, but the diffusibility of the phosphorus content appears to be reduced at 175° F., and that of the calcium content is diminished markedly at 125° F.

T. H. P.

Enzymic Conversion of Uric Acid into Allantoic Acid. R. Fosse, A. Brunel and R. de Græve. (*Compt. rend.*, 1929, **189**, 213–215.)—Many leguminous seeds are able to transform uric acid into allantoic acid, this change being effected by means of two enzymes. The first, an oxydase, like animal uricases, converts the uric acid into allantoin, which then fixes water under the influence of the second enzyme.

T. H. P.

Further Studies of the Chemical Nature of Vitamin *A*. J. C. Drummond and L. D. Baker. (*Biochem. J.*, 1929, **23**, 274–291.)—The unsaponifiable fraction from 125 gallons of high-quality medicinal cod-liver oil was submitted to fractional distillation at pressures of about 0·01–2 mm., but it was not found possible thereby to separate vitamin A. After removal of most of the cholesterol fractionating caused decomposition, with considerable loss of the vitamin. Separation of the constituents of the fraction by the preparation of phthalates or substituted phthalates was also impracticable, nor could information as to their nature be obtained by reduction with hydrogen in the presence of catalysts. The same difficulties were encountered with the unsaponifiable fraction from sheep-liver fat, and here decomposition was, at least partly, due to the presence of a highly unsaturated hydrocarbon somewhat resembling squalene. The unsaponifiable fractions of Greenland and Japanese shark liver oils consisted largely of selachyl, batyl, chimyl and oleyl alcohols, and distillation of the fractions was accompanied

by comparatively little destruction of the vitamin, probably owing to the small proportion of complex alcohols and hydrocarbons of the terpene series. It is concluded that vitamin *A* is present in such small proportions (probably less than 1 per cent.) in the unsaponifiable fraction that chemical means of separation are unlikely to succeed unless some characteristic derivative possessing properties suitable for isolation should be discovered. In support of this view, recognisable substances to the amount of 90–95 per cent. of the whole material were isolated from the unsaponifiable fraction of Japanese shark-liver oil, and, so far as could be ascertained, the residue consisted to a large extent of the same substances in less pure condition. The structure for chimyl alcohol as a monoglyceryl ether of cetyl alcohol has been confirmed. D. G. H.

Vitamin *B* Content of Polished Rice Koji. R. Takata. (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 188B.)—Rats fed with polished rice koji as the sole source of the vitamin attained 105 to 142 grms. in weight in 3 months, when growth stopped and their body weights began to decrease. Those fed with polished rice upon which *Aspergillus oryzae* had not grown died within 2 months. Pigeons fed with polished rice koji died in 30 to 41 days, whereas those fed with polished rice died in 23 to 35 days. It would therefore appear that polished rice koji contains very little vitamin *B*. R. F. I.

Agricultural.

Analysis of Tomato Plants, I. O. Owen. (*J. Agric. Sci.*, 1929, **19**, 413–432.)—In order to evaluate the part played by phosphates in tomato culture, the plants subjected to various treatments have been analysed for potash, phosphoric acid and nitrogen. Immediately after collection the material was freed from foreign matter, the green weight being recorded and the sample dried at 98–100° C. to constant weight, usually attained after 12 or 16 days. With old plants the dried stalks were cut up, the whole of the sample being ground in a porcelain mortar or a hand mill to pass a fine sieve. The nitrogen in 0·75–1 grm. of the dry tissue was determined by the Kjeldahl method, the amount of nitrate and other nitrogen to which this method is inapplicable being apparently negligible. For the determination of the ash, 2–3 grms. of material were heated at low redness to constant weight, the ash of foliage and stems being of a uniform grey colour. The fruit gave dark grey or black ash, but the amount of carbon present proved negligible. For the determination of potash and phosphoric acid, the weighed ash was dissolved in 10 per cent. hydrochloric acid, hydrogen sulphide being evolved with the ash of green tissue. The acid solution was heated to boiling and filtered into a measuring flask, the cold filtrate and washings being made up to volume. Aliquot parts were measured into silica dishes, and sufficient baryta solution to precipitate the sulphates, and also some calcium carbonate, were added. After the silica had been rendered insoluble, potassium was determined in the hot aqueous extract of the residue by the perchlorate method, and phosphoric acid in

the acid extract by precipitation as ammonium phosphomolybdate and weighing as the blue anhydride.

The results obtained show that the needs of the tomato plant for phosphates as a direct nutrient are low, but it is possible that lack of phosphate may reduce the intake of potash—supplied only as sulphate—and affect the flavour of the fruit. With unmanured plants the fruit is of inferior quality, but its weight is 2·6 times that of foliage and stems; with manured plants, which have a higher ash content, this ratio is 1·6. The actively growing parts of the plant are richest in the three nutrients, and the determination of these in grms. per plant for manured and unmanured plants, respectively, gave: Potassium oxide, 18·22 (2·775); phosphoric anhydride, 2·028 (0·9895); nitrogen, 9·324 (4·922). The percentage composition of the fresh fruit from manured (unmanured) plants was: Water, 93·5 (94·9); potassium oxide, 0·3237 (0·0556); phosphoric anhydride, 0·0491 (0·0355); nitrogen, 0·1591 (0·1769). T. H. P.

Cobaltinitrite Volumetric Method of Determining Potassium in Soil Extracts. G. Milne. (*J. Agric. Sci.*, 1929, **19**, 541–552.)—The platinichloride and perchlorate methods often yield unsatisfactory results when applied to the determination of the small proportions of potassium in soils. The cobaltinitrite method also presents difficulties, and in order to overcome these the following modified procedure has been devised. The reagents used are: Sodium nitrite, 100 grms. per litre; sodium chloride, saturated solution; cobalt chloride ($6H_2O$), 100 grms. per litre; acetic acid, 100 grms. per litre; sodium sulphate, 25 grms. per litre; glass dust, passing a 100-mesh sieve, in suspension in water; standard potassium permanganate solution, conveniently 0·05 *N*; standard oxalic acid, conveniently slightly stronger than 0·05 *N*, and containing 50 c.c. of sulphuric acid per litre. Freedom of the reagents from potassium must be ensured by satisfactory blanks. The solution prepared for analysis should be neutral and free from ammonium salts and organic matter, and the analysis should not be conducted where ammonia is being used. Aliquot parts representing up to 0·05 grm. of potassium oxide (requiring about 120 c.c. of 0·05 *N* permanganate) may be taken for the quantities of reagents specified, but from 0·005 to 0·025 grm. is most convenient.

The solution for analysis is reduced to about 10 c.c. in a 3-inch evaporating dish, 10 c.c. of the sodium chloride solution, 10 c.c. of the cobalt chloride solution, and 15 c.c. of the sodium nitrite solution being added in order, and the whole mixed with a short glass rod, which is left in the basin. The mixture is evaporated on a steam-bath to stiff pastiness or hard dryness, being well stirred occasionally, especially towards the end of the evaporation, to work the crystalline crusts into the liquid. After cooling (the analysis may be interrupted here), 10 c.c. of 10 per cent. acetic acid are well stirred in to assist solution of the excess of reagents and sodium chloride. After 15 minutes 10 c.c. of water are mixed in and the whole filtered through a small Gooch crucible charged with a disc of No. 40 Whatman paper, well pressed down at the edges and covered with a layer of the finer particles

of the glass dust. The precipitate is washed by decantation with 2·5 per cent sodium sulphate solution, transferred to the crucible, and washed six or eigh times with the same wash liquid; total washings need not exceed 25 c.c. (the analysi may be interrupted here). Allowing for an excess of at least 10 c.c., a measure quantity of 0·05 *N* permanganate is diluted and heated to boiling, about 10 c.c of dilute sulphuric acid added from a burette, and the solution again boiled an removed from the flame. The precipitate in its crucible is immediately added an stirred round well, and the beaker covered and left for 10 minutes. After 2 or minutes hydrated manganese dioxide separates and if left for longer than 15 o 20 minutes this may be slow in redissolving later. A measured volume of th standard oxalic acid, sufficient to give a perfectly clear solution, is now added and after removal of the crucible, the excess of oxalic acid is titrated with permanganate A complete blank analysis (better two or three) should be made for each new se of reagents and may with advantage be repeated from time to time during a lon series of analyses: 1 c.c. of 0·05 *N* permanganate corresponds with 0·000415 grm. o K_2O.

When this method is applied to citric acid soil extract, the organic matte may be removed either (1) by evaporation with nitric acid, followed by gentl ignition, the aqueous extract of the finely powdered residue being used for th analysis, or (2) by ignition without nitric acid, silica being then removed, and th residue again ignited and extracted with water. Either procedure gives 96–9 per cent. recovery of added potassium salt. Analyses of ammonium chlorid extracts gave unsatisfactory results, and attention is directed to the need for convenient means of destroying large amounts of ammonium salts in cases where an appreciably volatile constituent is to be estimated in the residue. T. H. P.

Detection of Castor Beans in Feeding Stuffs. M. Wagenaar. (*Z. Unters. Lebensm.*, 1929, **57**, 413–418.)—The detection of castor beans (*Ricinus communis minor* or *major*) in cattle foods is of importance on account of the poisonous nature of the toxalbumin. Kobert's biological method (*Chem. Ztg.*, 1913, **37**, 1282) in which an anti-ricin serum is used, is stated to be capable o detecting 0·1 per cent., but the blood agglutination method, though very sensitive, is easily upset by other constituents. Microscopically the bean is identified by a layer of short, black or dark-brown, 4- or 8-sided, slightly curved prismatic palisade cells, under a stratified spongy parenchyma immediately beneath the epidermis. They are very resistant to most reagents, but strong nitric acid readily separates them. In polarised light a fine, bright characteristic fringed edge is seen, and the cells, which are doubly refracting, show pale blue longitudinal and yellow latitudinal interference colours. To determine the proportion of castor beans from the area of these cells 1 grm. of the defatted sample is pulverised in an agate mortar to separate the calcium silicate. The fragments (less than 0·5 sq. mm. in size) are heated for 1 hour on the water-bath in a wide-necked flask with 4 grms. of potassium chlorate and 50 c.c. of 2 *N* hydrochloric acid, when the chlorine liberated serves to separate the palisade cell, which fall to the bottom. After the addition

of 50 c.c. of 4 *N* sodium hydroxide solution and a further hour on the bath, the liquid is decanted, the cells concentrated in a centrifuge, and suspended in a viscous medium such as invert sugar syrup prepared from 70 grms. of sucrose, 30 grms. of water and 1 grm. of citric acid. A drop is placed on a microscope slide (2·8 × 2·3 cm. × 0·5 mm.) so that 1 sq. mm. fills the field, and weighed, and the total surface of the cells measured. The cells from 1 grm. of sample have an area of 1500 sq. mm. Candle nut (*Aleurites triloba* or *moluccana*), which is little used in Europe, has similar cells which, however, occur in blocks and are bigger and seldom curved, and lack the characteristic edge of the castor bean cells. Up to 1·5 per cent. of castor bean was added to linseed, arachis and rape cakes and determined by this method, with an error of 0·05 to 0·15 per cent. J. G.

Organic Analysis.

Tests for Phenols involving the use of Hydrogen Peroxide. A. H. Ware. (*Pharm. J.*, 1929, **123**, 15.)—The hydrogen peroxide is either used as the principal reagent, or to hasten, accentuate or alter the effect of the principal reagent, such as dihydroxyacetone or formaldehyde. In one method the reagent consists of 1 c.c. of a 10 vol. solution of hydrogen peroxide made up to 50 c.c. with concentrated sulphuric acid, and more distinctive results are obtained than in the second method, where one drop of the aqueous solution of hydrogen peroxide is added to the phenolic solution in the strong acid. Apparently specific results are described for the catechins, catechol, phloroglucinol, resorcinol, thymol, and gallic acid. Hydrogen peroxide alone enables a distinction to be made between carbolic acid and the cresols, and between phloroglucinol, orcinol and resorcinol. The test for catechins may be successfully applied to the identification of gambier. D. G. H.

A Reaction of Resorcinol and a New Coloured Indicator. L. Bey and M. Faillebin. (*Comptes. rend.*, 1929, **188**, 1679–1681.)—Resorcinol reacts with aqueous ammonia solution in the presence of certain cations to give a blue coloration, and the colour is also produced in the presence of lead acetate or stannic chloride. The reaction is an oxidation, and the cation acts as a catalyst. The blue colour is due to an unstable combination of a colouring matter with one or more constituents present in the solution, and when isolated is irreversibly converted in ammoniacal solution to another blue colouring matter. The first colour is red in acid solution, green in a solution of P_H 9·18, and in ammoniacal solution of a higher P_H value is transformed into the second blue colouring matter, which is rose-red in acid solution. These colouring matters may be isolated by extraction of the acid solution with a solvent such as amyl alcohol, and subsequent shaking with a buffer solution of known P_H, preferably within the range of the indicator. The red-blue indicator is obtained unless the shaking is in an acid medium, in which case the red green indicator results. The P_H range for the red-blue indicator is 4·3 to 5·9, the intermediate tints being violet. D. G. H.

Micro-Method for Determining Semicarbazones and its Application to the Analysis of Ketones. R. P. Hobson. (*J. Chem. Soc.*, 1929, 1384–1385.)—Solutions of semicarbazone or semicarbazide are hydrolysed if boiled under a reflux condenser with 15 per cent. of hydrochloric acid and 5 per cent. of mercuric chloride for 8 and 6 hours, respectively, the function of the latter being to oxidise the hydrazine formed and so prevent the production of ammonia by interaction with organic substances (*e.g.* sucrose, free ketones):—(1) $NH_2.CO.NH.NH_2+H_2O=NH_3+CO_2+N_2H_4$, (2) $N_2H_4+2HgCl_2=N_2+2Hg+4HCl$. If about 10 mgrms. of sample are used, the ammonia may be determined by means of Pregl's micro method, the liquid being made alkaline with a mixture of equal volumes of 40 per cent. sodium hydroxide and saturated sodium thiosulphate solutions. The latter serves to decompose the mercury and ammonium complex. The method has also been applied to ketones which may be converted quantitatively into semicarbazones, though excess of semicarbazide reagent must first be removed by precipitation of the semicarbazone with water, or by extraction of the semicarbazide by washing it with water from the evaporated mixture, or by extracting the residue with ether and shaking the ethereal solution with water. J. G.

Inorganic Analysis.

The Benzidine Colour Reaction of Japanese Acid Clay. N. Kameyama and S. Oka. (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 87B.)—The benzidine colour reaction was carried out in the complete absence of oxygen and still gave a positive result. The oxidising constituent of the clay can be removed by boiling it with 6 *N* hydrochloric acid for 30 hours. Evidence was found that Japanese acid clay also exerts an oxidising effect, though to a minor degree, by acting as a catalyst in the presence of oxygen. R. F. I.

Synthetic Japanese Acid Clay. N. Kameyama and S. Oka. (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 99B.)—The oxidising power, in which property the previously described synthetic clay (ANALYST, 1929, 65) was lacking, is supplied by adding 0·1 per cent. of manganese dioxide. This product then possesses all the known properties of the natural clay, though in some cases to a somewhat less degree. The blue coloration on contact with liver oil was less pronounced than that produced by the Japanese acid clay. (*Cf.* ANALYST, 1927, 553, 559.) R. F. I.

Genesis of Japanese Acid Clay. K. Kobayashi and K. Yamamoto. (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 174B.)—The authors have observed that acid clay is exclusively found along an intrusion of liparite through the Pliocene. The view is put forward that Japanese acid clay is a decomposition product of soda felspar and sodium silicate interposed between pre-tertiary strata and the liparite, the decomposition being effected by upgushing gases (carbon dioxide, sulphur dioxide, hydrogen sulphide, and steam), and a gel of hydrated aluminium silicate being formed. R. F. I.

Physical Methods, Apparatus, etc.

Testing Seeds, etc., under the Quartz Mercury Vapour Lamp. A. Niethammer. (*Z. Unters. Lebensm.*, 1929, **57**, 354–358.)—In certain cases the mercury vapour lamp may be used to distinguish fresh and sound seeds from old and damaged material, but it can be considered only as a guide, particularly when applied to identify seeds of different types. Fresh intact *Cannabis sativa* and *Ervum lens* give green colours, and old samples a matte-white. For *Lupinus albus* a grey brown colour is obtained, varying towards a yellow shade in old samples. *Pisum sativum* shows a lilac luminescence with red stripes which are absent from old samples, whilst *Phaseolus vulgaris* and *Vicia sativa* are lilac and bright green, respectively, if fresh, but show no colour if old. *Vicia faba* and *Linum usitatatssimum* vary from dark blue or lilac to pale yellow according to age. *Agrostemma githago, Sinapis alba, Brassica nigra, Ricinus communis, Secale cereale, Triticum sativum, Hordeum vulgare* and *Fagopyrum* all give lilac colours, new and old samples being indistinguishable. Walnut, hazel nut and almond give lilac colours when fresh and yellow when old, and coconut a characteristic lilac which is absent from old samples (*cf.* Popp, ANALYST, 1926, **51**, 540). J. G.

Reviews.

THE CHEMISTS' YEAR BOOK, 1929. Edited by F. W. ATACK, D.Sc., F.I.C. Pp. 1185 and Index. Manchester: Sherratt & Hughes. Price 21s.

The present edition of this work is the fourteenth to be published, and the annual appearance of the volume affords every indication of its utility. No new section has been included in the new volume, but the chapters on "Dairy Chemistry" have been re-written by Elsdon and Stubbs, two well-known authorities in this country. The number and variety of subjects with which the work deals is very large, each section having an importance dependent on the nature of the work of a particular chemist. The work is convincing of the marked progress which has been made in all domains of chemistry, and a glance at the pages of the volume is impressive, as it shows the almost innumerable subjects with which the chemist has to deal.

The article on "Qualitative Analysis. Dry-way Tests" occupies rather more than nine pages, but who would dare to suggest their suppression? Do they not convey the mind back to early schooldays, when troubles of a chemical nature were very real? The forward trend of science has, however, left most laboratories without "a charcoal block with a clean cavity in which to heat a substance in an oxidising flame," but this can be remedied.

The British Pharmacopoeia limits for lead and arsenic are set out in a convenient tabular statement, but, somewhat unfortunately, the prescribed tests of the U.S.P. are not given, but only a reference to Part II of that work which contains the tests. The U.S.P. is not always available.

The section on "Dairy Chemistry" states that the condition of sour milk may be improved by the addition of ammonia. It should be noted that the addition of ammonia to sour milk does not prevent the loss of solids on evaporation, and that, unless neutralisation has been effected with soda or strontia, the result obtained for total solids will be low.

The section devoted to "Agricultural Chemistry" has been written by no less an authority than Sir E. J. Russell, F.R.S. He deals very ably with the analysis of soils, and then passes on to the examination of fertilisers and, subsequently, to feeding stuffs. Unfortunately, the official methods of analysis given for both fertilisers and feeding stuffs are those which were contained in the Fertilisers and Feeding Stuffs Regulations, 1908; these were superseded by Regulations dated May, 1928. The processes given are, therefore, now, not necessarily official, and, further, the chapter obviously contains no mention of alternative processes included in the more recent Regulations. It is most desirable that the methods of analysis for feeding stuffs should be brought up to date without delay. The revision of the processes relating to the determination of oil and fibre, in particular, is most important, because of the differences in results which may be obtained by the old and new methods.

The only portion of the book which appears to remain stationary in length is the index. Somewhat unfortunately, the index only extends to sixteen pages, as it did twelve years ago. To a busy man, the utility of any work must depend to a large extent on the ease with which information can be run down in the text. The index might well be made more complete.

The work claims the highest commendation, and, generally, the analyst requiring information would not appeal to its pages without profit.

F. W. F. ARNAUD.

PHOTOMETRIC CHEMICAL ANALYSIS. Vol. II. NEPHELOMETRY. By JOHN H. YOE, Ph.D., with contributions by HANS KLEINMANN, M.D., Ph.D. Pp. xvi+337. London: Chapman & Hall, Ltd. Price £1 2s. 6d. net.

This is the complementary volume to the one on "Colorimetry" reviewed in THE ANALYST last March, and like the companion volume it is well produced. The subject is new, so much so that, save for some suggestive preliminary work by Mulder in 1859, its foundations were not laid until 1894, when Stas and T. W. Richards independently investigated its possibilities in atomic weight work. To the latter belongs the honour of having established the method, and to Kober the credit for its further development since 1912; precision instruments belong to the present decade. Thanks are due to the author for having narrated the history in

detail, while memory is fresh, and also for having entered into minutiæ of the instruments and their operation. This is good in a first general treatise, but in the next edition, which there is good reason to anticipate, the same information could be imparted more concisely to the advantage of the reader. A tendency to prolixity is evident throughout the book.

A far more serious weakness is in the arrangement of the work. The reader has presented to him the several nephelometers, the construction, operation and care of precision instruments, the theory of nephelometry, and is lead on to the practice of the art without being made acquainted with the general principles of the subject. It is not until he reaches Chapter V on the theory that the reader becomes aware of how the incident light is projected into the liquid, save only as far as general intelligence and experience assist him. A good general introduction describing the fundamental principles, a typical nephelometer, how to use it and the purposes to be served in academic and technological practice, would have made the following chapters much more easily readable.

The text fails of good expression in places; for example: "The theory of nephelometry may be defined as an explanation of the scattered visible light coming at right angles from an illuminated column of suspended substance and of the relationship between the intensity of scattered or reflected light and the concentration of the suspended particles." "The property of suspended substances scattering light is called Tyndall effect." (Page 48.)

On comparing the list of elements and substances to be determined by nephelometry in Vol. II with that of those to be quantified colorimetrically in Vol. I, one is impressed by so little overlapping. The six chapters on Inorganic Elements refer to Ammonia, Arsenic, Calcium, Chlorine, Phosphorus, and Sulphur; and the eleven chapters on Organic to Acetone, Amylase, Dichloro-Ethylsulfide, Fats, Oils and Fatty Acids, Lipase, Nucleic, β-Oxybutyric Acid, Pepsin, Proteins, Purine Bases and Trypsin. An attractive chapter to the practising analyst is the one on Ammonia, which describes how the nitrogen in an organic substance may be determined by the usual Kjeldahl digestion in Sulphuric Acid followed by simple dilution, the addition of reagents, and matching the cloud against that produced in a standard Ammonium Sulphate solution.

Other chapters which make a similar appeal are those referring to Pepsin, Proteins and the like. Simple nephelometric methods may replace the difficult chemical separations; thus "From two to three days are required for the determination of casein, globulin and albumin in milk when it is done by the usual technique, whereas with the nephelometric method it can be done in twenty to thirty minutes." (Page 256.)

The author's very carefully prescribed directions indicate the need for close attention to detail as a necessary condition for obtaining precise results, but this should not discourage a wide use of the method for both precise and approximate determinations according to requirements; no doubt approximate work will meet

the needs of much control work, and prove very convenient in practice. The author would have strengthened his advocacy of so new a method had he given more information as to how results so obtained compare with those following from the better known methods.

The volume closes with a good classified bibliography, which is better arranged than is that in Vol. I.

S. JUDD LEWIS.

Publications Received.

INDEX TO THE LITERATURE OF FOOD INVESTIGATION. No. 1. Department of Scientific and Industrial Research. Compiled by AGNES ELIZABETH GLENNIE, B.Sc. H.M. Stationery Office. Price 2s. net.

Historical review of earlier papers—Classified summary of more recent papers and patents:—I, Meat; II, Pig flesh; III, Poultry and game; IV, Fish; V, Eggs; VI, Dairy produce; VII, Fats and oils; VIII, Fruit and vegetables; IX, Grain, crops and seeds; X, Theory of canning; XI, Theory of freezing and chilling; XII, Bacteriology; XIII, Mycology; XIV, Engineering; XV, Miscellaneous.

ANNUAL REPORT OF THE MEDICAL OFFICER OF HEALTH FOR LONDON FOR 1928, TOGETHER WITH THE REPORT OF THE PUBLIC ANALYST.

ANNUAL REPORT OF THE MEDICAL OFFICER OF HEALTH FOR LEICESTER FOR 1928, TOGETHER WITH THE REPORT OF THE PUBLIC ANALYST.

ANNUAL REPORT OF THE CHEMICAL EXAMINER TO THE GOVERNMENT OF MADRAS.

REPORT OF THE DEPUTY CITY ANALYST FOR BIRMINGHAM, FOR THE SECOND QUARTER, 1929.

HANDBUCH DER BIOLOGISCHEN ARBEITSMETHODEN (ABDERHALDEN). Abt. IV: QUANTITATIVE STOFFWECHSELUNTERSUCHUNGEN. F. G. BENEDICT. Berlin: Urban & Schwarzenberg. Price 4 marks.

HYDROGEN IONS. By H. T. S. BRITTON, D.Sc. London: Chapman & Hall. Price 25s. net.

DIE ROLLE DER ZYKLISCHEN AMINOSÄUREANHYDIDE IN DER NEUEREN STRUKTURCHEMIE DER PROTEINE. By E. KLARMANN. Berlin: Urban & Schwarzenberg. Price 9 marks.

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