THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, May 4th, the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read for the first time in favour of Charles Carr Marginson, B.Sc., A.I.C., Ph.C., Wilfred Mather, A.M.C.T., F.I.C., Alec Duncan Mitchell, D.Sc., F.I.C., and M. Niyogi, M.Sc.

Certificates were read for the second time in favour of Reginald Haydn Hopkins, D.Sc., F.I.C., and William Basil Walker, B.Sc., A.I.C.

The following were elected Members of the Society:—Edward Bertram Anderson, M.Sc., F.I.C., Edward Foster Eaton, Frank Maudsley, B.Sc., F.I.C., Samuel Gordon Stevenson, B.Sc., B.Pharm., F.I.C., and James William Thom, B.Sc.

The following papers were read and discussed:—"The Quantitative Separation of Tantalum, Niobium, Titanium and Zirconium, and a New Analytical Grouping," by W. R. Schoeller, Ph.D., and A. R. Powell (*Work done under the Analytical Investigation Scheme*); "The Iodine and Thiocyanogen Values of Irish Butter," by P. S. Arup, M.Sc., F.I.C.; "Sediments in Ink and in Writing," by C. Ainsworth Mitchell, D.Sc., F.I.C., and T. J. Ward; and "The Determination of Minute Amounts of Copper in the Presence of Iron and certain other Metals," by L. G. Haddock, B.Sc., and Norman Evers, B.Sc., F.I.C.

Death

WITH great regret we record the death, on May 23rd, of Dr. J. C. Thresh. An obituary notice will be published later.

Phloroglucinol Method for the Determination of Mechanical Wood Pulp in Paper

By H. B. DUNNICLIFF, M.A., Sc.D., F.I.C., and H. D. SURI, M.Sc.

(*Read at the Meeting, February* 3, 1932)

The determination of mechanical wood pulp (M.W.P.) in cheap newsprint has been attempted by various physical (optical) and chemical methods. Of the latter, the volumetric phloroglucinol method of Cross and Bevan (*Papier Ztg.*, 1907, **32**, 4113, 4479) is the most accurate quantitative method proposed. The details of this may be found in standard analytical text-books [*cf. Allen's Commercial Organic Analysis*, Vol. I (1923), p. 626].

In India this method did not give reliable results, and we have attempted to find (*a*) the effect of temperature on the result; (*b*) the relationship between the volume of standard reagent and the weight of paper necessary for quantitative action; (*c*) the time required for quantitative action; and (*d*) the mechanism of the reaction.

The formula of Cross and Bevan for the calculation of the percentage, H, of M.W.P. in paper depends upon the terms, x, y and z in the equation:

$$H = \frac{100\,(x - y)}{z - y} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

in which y, z and x are the weights of crystalline phloroglucinol required to react with 100 grms. of chemical pulp, mechanical wood pulp and pulp in the samples under examination, respectively.

As a result of many experiments, Cross and Bevan gave $y = 1$ and $z = 8$ as average values for these terms, though other workers have proposed figures which differ more or less widely from them.

In India, where high temperatures are ordinarily prevalent, reliable results cannot be guaranteed if a hydrated compound which has an appreciable vapour pressure is adopted as the weighed fundamental criterion. For this reason, in the work to be described, anhydrous phloroglucinol, obtained by heating the hydrated compound at 110° C., was used throughout. That the dehydrated compound does not undergo any constitutional change in the drying process (other than the loss of water) was shown by the fact that equal volumes of equivalent solutions of hydrated and dehydrated phloroglucinol required the same quantity of standard formaldehyde solution for complete interaction, as represented by the equation:

$$2C_6H_3(OH)_3 + HCHO = CH_2:(C_6H_2(OH)_3)_2 + H_2O \qquad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

Accepting the form of Cross and Bevan's equation and writing it

$$H = \frac{100\,(x - \alpha)}{\beta - \alpha} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

in which α, β and x are the weights of anhydrous phloroglucinol required to react with 100 grms. of chemical pulp, mechanical wood pulp, and pulp in the unknown sample, respectively, the values of α and β had to be determined.

"Absorption Value."—Throughout this report the amount of phloroglucinol removed from the solution by a paper or pulp is referred to as the amount "absorbed." As shown in the sequel, this includes phloroglucinol removed both by chemical action and by adsorption. The "absorption value" is the number of grms. of anhydrous phloroglucinol absorbed by 100 grms. of dry ash-free paper or pulp.

Time.—As regards the time required for quantitative reaction, it may be stated that the reaction is found to be complete after 12 hours at 35° C., the standard temperature decided upon for the operation (*vide* p. 356). Since, however, working conditions made this period rather awkward, the time proposed by Cross and Bevan, *i.e.* 18 hours, was uniformly adopted. Bottles were usually placed in the bath at 5 p.m. and removed at 11 a.m. next day.

Determination of the Absorption Factors.—A constant amount (1 grm.) of each kind of dried pulp was treated with varying quantities of 0·5 per cent. anhydrous phloroglucinol in hydrochloric acid (12 per cent.) for equal periods of time. Flasks containing the reaction mixture were rotated under water in an electrically regulated thermostat capable of being controlled to $\pm 0{\cdot}1°$ C.

For these experiments, formaldehyde solution was made up as prescribed by Cross and Bevan (*loc. cit.*), and the titration was carried out as formulated by them. The determination of the end-point (cheap newsprint being used as indicator) was carried out in the last stages by "triple spotting," *i.e.* putting a drop three times on the same spot on the paper and drying after the placing of each drop, as described by Cross and Bevan.

Table I

Absorption Factors

Showing the effect of the quantity of anhydrous phloroglucinol and of temperature on the absorption values of Amsterdam pulps.

Volume of solution per grm. of pulp c.c.	At 20° C.	At 25° C.	At 30° C.	At 35° C.
	A. *Chemical Pulp* (*S.P.*)			
20	0·79	0·90	1·04	1·14
30	0·84	1·03	1·17	1·16
40	0·86	1·13	1·16	1·21
50	0·90	1·21	1·18	1·22
100	0·91	1·20	1·21	1·21
	B. *Mechanical Wood Pulp* (*M.W.P.*)			
20	5·26	6·27	6·45	7·09
30	5·61	6·70	6·95	7·86
40	6·12	7·20	7·43	8·51
50	6·65	7·22	7·65	8·52
100	7·34	7·43	7·67	8·60
150	7·40	—	—	—
200	7·30	—	—	—

These figures show (1) that the absorption values of S.P. and M.W.P. for 0·5 per cent. (anhydrous) phloroglucinol solution increase with the increase of the volume of phloroglucinol solution used to react with a constant weight of pure pulp in each case, and (2) that at different temperatures different maximum absorption values are obtained. These are realised at 25°, 30° and 35° C. if 1 grm. of paper is treated with 50 c.c. of the phloroglucinol solution. At 20° C. a much greater volume of this reagent is required for complete reaction.

Hence, the original method, in which 2 grms. of paper or pulp are used with 40 c.c. of 0·5 per cent. crystalline phloroglucinol solution (=0·389 per cent. anhydrous phloroglucinol), at ordinary European temperatures would fail to effect the maximum absorption which the successful operation of this method demands. We find that the factors of Cross and Bevan are valid, and give good results with mixtures of a limited range of composition and at low temperatures, but that they are not valid for wide ranges of composition or temperature, or for the fixed high temperature which it is necessary for the analyst in India to employ for the sake of uniformity at different places.

It is imperative, therefore, that analyses should be made under carefully specified conditions. These require that (1) a fixed amount of paper should be treated with (2) a fixed volume of standard phloroglucinol solution, which shall be (3) sufficient to give maximum absorption (4) at a particular temperature, and (5) for a definite period of reaction. These factors should also be independent of the percentage of mechanical wood pulp present in the paper.

Results with Artificial Mixtures.—To illustrate the above statement, artificial mixtures of the two pulps were exposed to the action of 100 c.c. of phloroglucinol solution at 20° C. (to give maximum absorption), and the results in Table II were obtained.

Table II

Temperature 20° C.

M.W.P. in mixture Per Cent.	Absorption value	M.W.P. (calc.). Constants (*vide* Table I) $\alpha=0{\cdot}91$ and $\beta=7{\cdot}34$ Per Cent.
80	6·10	80·7
60	4·86	61·4

An error of 1 to 1·5 per cent. would be accounted for by a difference of one drop (0·05 c.c.) of formaldehyde in the titration reading. The time required to titrate volumes of solutions greater than the 10 c.c. ordinarily used was excessive.

It is essential, therefore, that determinations should be carried out at a temperature easily attainable at all seasons, and that a concentration of phloroglucinol should be adopted which would give a maximum absorption at that temperature. The temperature finally selected was 35° C., although that is occasionally lower than laboratory temperature (temperatures up to 40° C. have been recorded), and the absorption values of S.P. and M.W.P. from different sources were determined when 1 grm. of the pulp was exposed to the action of 50 c.c. of 0·5 per cent. anhydrous phloroglucinol solution (*vide* Table III).

TABLE III

ABSORPTION FACTORS OF PHLOROGLUCINOL AT 35° C.

Quality.	S.P.	M.W.P.
1. Amsterdam	1·26	8·54
2. Norwegian	1·10	8·68
,, (paper form)	—	8·48
3. Boregard	—	8·72
4. Finska	—	8·48
5. Swedish	1·20	—
	Mean=1·187	Mean=8·57

ABSORPTION VALUES OF PULPS AND PAPER OF KNOWN COMPOSITION.—Table IV gives the absorption values and compositions of certain pulps and specially made standard papers of known composition, together with the calculated composition, the absorption values shown in Table I being used for 50 c.c. of solution to 1 grm. of pulp at various temperatures. In these cases the ash was negligible.

TABLE IV

ABSORPTION OF ANHYDROUS PHLOROGLUCINOL BY STANDARD PAPERS AND KNOWN MIXTURES (A.M.) AT VARIOUS TEMPERATURES

	Composition of standard paper and artificial mixtures		25° C.		30° C.		35° C.	
	M.W.P. Per cent.	S.P. Per cent.	Absorption per 100 grms. of paper	Calc. per cent. of M.W.P. consts. $\alpha=1{\cdot}21$ $\beta=7{\cdot}22$	Absorption per 100 grms. of paper	Calc. per cent. of M.W.P. consts. $\alpha=1{\cdot}18$ $\beta=7{\cdot}65$	Absorption per 100 grms. of paper	Calc. per cent. of M.W.P. consts. $\alpha=1{\cdot}22$ $\beta=1{\cdot}52$
A.M.	80	20	—	—	—	—	7·02	79·5
Paper	75	25	—	—	—	—	6·78	76·1
,,	70	30	5·38	69·4	5·82	71·7	6·39	70·8
,,	60	40	4·69	58·0	5·13	61·1	5·38	59·7
,,	50	50	4·18	49·5	4·41	49·9	4·85	49·7
A.M.	40	60	—	—	—	—	4·20	40·8

STUDY OF THE MECHANISM OF THE REACTION BETWEEN MECHANICAL WOOD PULP AND PHLOROGLUCINOL AT 35° C.—One grm. of the mechanical wood pulp was exposed in a series of stoppered bottles to the action of the same volume of phloroglucinol solution of different concentrations in a thermostat at 35° C. for 18 hours. The contents were then filtered and titrated against formaldehyde as before. The results are given in Table V.

TABLE V

	Amount of Phloroglucinol		
	In 50 c.c. of original solution Mgrms.	Absorbed by 1 grm. of M.W.P. $= C_s$ Mgrms.	Remaining in 50 c.c. of solution after equilibrium $= C_e$ Mgrms.
1.	25·0	20·0	5·0
2.	50·0	40·0	10·0
3.	75·0	50·8	24·2
4.	100·0	60·0	40·0
5.	112·5	64·5	48·0
6.	125·0	67·8	57·2
7.	137·5	71·0	66·5
8.	150·0	73·5	76·5
9.	162·5	75·0	87·5
10.	175·0	77·0	98·0
11.	187·5	78·4	109·1
12.	200·0	80·0	120·0
13.	212·5	81·8	130·7
14.	225·0	83·2	141·8
15.	237·5	85·4	152·1
16.	250·0	87·2	162·8

The curve obtained by plotting C_e against C_s resembles a typical adsorption isotherm, which is usually represented by the relationship:

$$C_s = K \times C_e^{\frac{1}{p}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$\text{or} \quad \log C_s = \frac{1}{p} \log C_e + \text{constant} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The values of the constants in (4) in this case are $K = 4{\cdot}40$ and $p = 4{\cdot}15$.

Hence, if $\log C_e$ is plotted against $\log C_s$, a straight line should result, and, with the exception of No. 1, this is the case with the values given in Table V. Since the value for No. 1 does not fall on the straight line, it appears that the results are affected by some other influence. This may be due to a chemical action which takes place predominantly in the early stages of the action between the lignin of the mechanical wood pulp and the phloroglucinol.

The extent to which chemical action takes place was shown by exposing 1 grm. of M.W.P. to 50 c.c. of 0·5 per cent. of phloroglucinol solution for 20 hours at 35° C. The pulp (which had taken up 0·0870 grm. of phloroglucinol) was then repeatedly extracted with 12 per cent. hydrochloric acid (sp.gr. 1·06) at 35° C., until the extracts showed negligible tests for phloroglucinol.

Determinations of the phloroglucinol in the collected extracts showed that 0·0677 grm. of the phloroglucinol was not removable from the solid phase, *i.e.* it had presumably entered into chemical combination with the lignin of the M.W.P. Thus, in addition to the 0·0677 grm. of phloroglucinol which takes part in the chemical reaction, 0·0193 grm. of phloroglucinol is retained by each gram of M.W.P. in some physical condition.

THE VELOCITY OF THE REACTION.—An attempt was made to determine the velocity at which the chemical reaction proceeds and the order of the reaction. A number of bottles, each containing 1 grm. of M.W.P. and 50 c.c. of phloroglucinol solution, were rotated in a thermostat at 35° C., and the reaction was stopped after definite intervals of time. The results are shown in Table VI.

TABLE VI

SHOWING THE AMOUNT OF PHLOROGLUCINOL WHICH HAD REACTED WITH 100 GRMS. OF M.W.P. AFTER THE INTERVALS OF TIME SHOWN IN COLUMN ii

Total amount of phloroglucinol available = 25 grms.

i	ii	iii	iv	v	
No.	Time in hours	Phloroglucinol removed from the solution in grms.	$\frac{1}{t}\log\frac{a}{a-x}=K$	$\frac{1}{t+2\cdot3}\log\frac{a}{a-x}=K_1$	
	$=t$	$=x$	$a=25$	$a=25$	
1.	0·25	4·372	0·3336	0·0327	
2.	0·50	4·950	0·1916	0·0342	
3.	0·75	5·166	0·1340	0·0329	Mean=
4.	1·00	5·279	0·1030	0·0312	0·0328
5.	1·50	6·270	0·0836	0·0330	
6.	2·00	6·518	0·0656	0·0305	
7.	2·50	6·766	0·0545	0·0285	
8.	3·00	7·096	0·0484	0·0273	
9.	4·00	7·474	0·0386	0·0245	

The high initial value of x shows that there is a very rapid reaction at first which it is not possible to measure. Assuming that the reaction is unimolecular (or bimolecular), we can determine the time, t_1, which the amount of change represented by the initial rapid action would have taken if the reaction had proceeded with a normal velocity from the start.

The method of calculation is shown in detail by Dunnicliff and Butler (*J. Chem. Soc.*, 1921, **119**, 1384) for a homogeneous system, and, for a heterogeneous system, by Dunnicliff, Suri and Malhotra (*J. Chem. Soc.*, 1928, 3106). The value of t_1 has been determined by equating pairs of expressions

$$\frac{1}{t+t_1}\log\frac{a}{a-x}$$

for various values of t and x from data shown in Table VI, experiments (1) to (5).

The mean of six such calculations gave $t_1 = 2{\cdot}3$ hours. The values found for the constant, K_1, for a unimolecular reaction are recorded in column v of Table VI, and show a reasonable constancy round the mean value $K_1 = 0{\cdot}0328$. Calculation as for a bimolecular reaction does not give a more constant value for K or K_1. These results indicate that for a period of about 1·5 hours (corrected time including the abnormal period = 3·8 hours) the reaction is unimolecular.

The velocity of the reaction then slows down until, after about 8 or 9 hours (actual time), it is nearly negligible.

The curve found by plotting C_e against C_s (Table V) is indicative of adsorption, and the conclusion one must deduce from the two sets of results is that adsorption precedes chemical action (which is most rapid at first), and that there is some definite relationship between the chemical action and adsorption phenomena. This is borne out by the fact that, although much of the adsorbed phloroglucinol enters into irreversible chemical combination with a component of the M.W.P., the form of the curve remains unchanged.

Since the reaction involves both chemical action and adsorption proceeding side by side, it is clear that the only prospect of obtaining satisfactory results in the determination of M.W.P. in paper by this reaction depends upon having conditions clearly defined as set forth on p. 356. It is also essential that sufficient excess of reagent should be used to supply adequate phloroglucinol for the balanced system (represented by chemical combination and adsorption) to be in equilibrium with the solution left after giving the necessary amount of phloroglucinol to that system. These conditions must be realisable for papers containing widely different percentages of M.W.P.

We and other chemists in this laboratory have analysed several hundreds of samples of paper, both commercial varieties and papers specially made as standards, and have found that, for the papers of known composition, the following procedure gives results accurate to about 1 per cent.

DETERMINATION OF MECHANICAL WOOD PULP IN PAPER.—About 6 to 8 grms. of paper are cut from different parts of the sheet or sheets under examination. These are rolled into a packet and suspended by a thread beneath a reflux condenser inside a conical flask containing 50 c.c. of 90 per cent. alcohol. The flask is then heated on a water-bath for 2–3 hours, or, with coloured paper until as much as possible of the colour is removed. This treatment also removes a portion of the sizing materials. The paper is now drained, cut into small pieces (about 3–4 mm. square) and dried to constant weight at 100° C.

Correction for Mineral Loading.—Since the percentage of M.W.P. on the fibre content of the paper is usually required, the percentage of loading material in the paper must be determined and a correction applied. For this purpose, about 2 grms. of the dried paper are "ashed," and the amount of the incombustible and non-volatile residue is accepted as a measure of the mineral loading material present.

Determination of "Absorption Value."—To determine the "absorption value," 1 grm. of the dried paper is placed in a clean, dry, glass-stoppered 4-ounce bottle; 50 c.c. of the standard phloroglucinol solution (0·5 per cent.) are added from a pipette, and the bottle is sealed with wax. After being shaken several times to cause the pieces of paper to sink to the bottom, the bottle is placed in a thermostat at 35° C. (±0·1° C.) for 18 hours. The contents of the bottle are rapidly filtered through a cotton-wool plug into another clean dry bottle, supported in the thermostat at the same temperature. The solution is then cooled to room temperature, 10 c.c. are measured into a conical flask, 20 c.c. of hydrochloric acid

(12 per cent., sp.gr. 1·06) are added, and the titration is carried out as described by Cross and Bevan. As a control, 10 c.c. of the standard phloroglucinol solution are then titrated under identical conditions. The difference between the volume of formaldehyde solution required for the control and the volume required for the solution which has reacted with the paper, multiplied by 5, is a measure of the phloroglucinol which has been taken up by 1 grm. of the paper. From this the weight of phloroglucinol is determined in grms. and, when multiplied by 100, this gives the value of x in the equation:

$$H = \frac{100 \times \left(\frac{100x}{100\text{—per cent. of ash}} - 1{\cdot}20\right)}{8{\cdot}56 - 1{\cdot}20} \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

$$\text{or} \quad H = 13{\cdot}587 \times \left(\frac{100x}{100\text{—per cent. of ash}} - 1{\cdot}20\right) \ldots\ldots\ldots\ldots \quad (7)$$

In the determination of M.W.P. in commercial papers a blank test was always carried out on a standard paper of approximately the same M.W.P. content, as determined by the Spence and Krauss optical method. A correction may be applied to compensate for the possible error referred to on p. 360.

We wish to acknowledge the assistance of the late Lala Kishen Lal, M.Sc., who did useful work in the early stages of this investigation by analysing many samples, and of Lala Kishen Prasad, M.Sc., who also carried out a number of analyses and commenced an investigation on the influence of fillers, sizing and dyes on the validity of the method. The results of that investigation are not yet sufficiently definite for inclusion in this paper.

Funds for this investigation were provided by the Central Board of Revenue, and this paper is published with the permission of the Government of India.

Central Board of Revenue,
Control Laboratory, Lahore, India.

Some Analytical Applications of Sodium Hydrosulphite. II*

Separation of Tin from Copper, Zinc, Lead, etc., and from Oxalic Acid

Determination of Tin in Steel

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

(*Read at the Meeting, February* 3, 1932)

It was shown in the first part of this paper (Analyst, 1929, **54**, 395) that certain metals, *e.g.* antimony, lead and bismuth, could be precipitated as metal from a hot alkaline cyanide solution by treatment with sodium hydrosulphite and thus be separated quantitatively from, *e.g.* copper. Tin under these conditions does not precipitate as metal; if, however, an excess of ammonium salts is present, ensuring the absence of alkali other than ammonia, a chocolate brown precipitate, apparently stannous sulphide, is thrown down on boiling; this reaction, which is only partial, seems to depend on the formation of sulphide, owing to the break-up of the sodium hydrosulphite molecule; it will be remembered that cadmium under the same conditions may be deposited partly or entirely as yellow cadmium sulphide. If ammonium sulphide is added to the solution before the hydrosulphite, the reaction proceeds to completion, and, since stannous sulphide is quite insoluble in ammonia or ammonium sulphide, and the precipitate is very dense and powdery, it forms a clean and rapid method of separating tin from various metals whose sulphides are soluble in alkali cyanide, and which are not precipitated as metal by hydrosulphite under these conditions, notably copper, iron, nickel, and zinc.

Process.—In the absence of large amounts of interfering metals (*e.g.* copper, lead, zinc, etc.), the solution containing the tin is treated with excess (say 10 c.c.) of citric acid solution (100 grms. dissolved in 200 c.c. of water), and made alkaline with ammonia; 10 c.c. of potassium cyanide solution (saturated), 25 c.c. of ammonium chloride solution (20 per cent.) and 10 c.c. of ammonium sulphide are then added, followed by about 7 grms. of sodium hydrosulphite, and the solution is boiled for one minute; at the end of this time it is allowed to stand for a minute or so to let the temperature drop just below boiling point, 2 or 3 grms. more of sodium hydrosulphite are added, and the flask is allowed to stand for about 15 minutes on the steam-bath. The liquid is next filtered, hot, through a closely-packed pulp filter, the precipitate is washed, with as little delay as possible, four

* Communication from the Research Department, Woolwich.

times with an almost boiling 5 per cent. solution of ammonium chloride, containing 10 c.c. of potassium cyanide solution (saturated) and 2 or 3 grms. of sodium hydrosulphite per 200 c.c. (this treatment is to remove any traces of copper, zinc, iron, etc., which may be present), and then three times with hot 5 per cent. ammonium chloride solution.

The precipitate now contains all the tin, all the lead and bismuth and most of the antimony contained in the original solution, none of which metals in moderation interfere with the final determination of the tin, but it is free from copper, nickel, iron, zinc, etc., some of which interfere very seriously with the volumetric determination. The pulp (with the precipitate) is shaken into a beaker and treated with a mixture of 10 c.c. of sodium hydroxide solution (20 per cent.) and 20 c.c. of hydrogen peroxide, which is used to rinse down the sides of the funnel and beaker; the pulp is thoroughly broken up with a glass rod, the liquid is heated nearly to boiling, and, after the addition of 30 c.c. of citric acid solution (100 grms. in 200 c.c. of water), it is boiled for a few moments; the solution is next filtered from the pulp through a very small pulp filter into a beaker, and the pulp is pressed down with the glass rod and thoroughly washed with hot water.

The filtrate is evaporated to about 25 c.c., cooled, poured into a measuring cylinder, and roughly measured; it is then poured into a 750-c.c. conical flask and rinsed in with an approximately equal volume of strong hydrochloric acid, and the beaker and measuring cylinder are finally rinsed in with repeated quantities of dilute (1:1) hydrochloric acid, sufficient in all to bring the total volume in the flask up to about 100 c.c.; about 4 grms. of sodium hypophosphite and 1 c.c. of saturated mercuric chloride solution are added, and the mouth of the flask is closed with the attachment for tin titrations described in former papers (Evans, ANALYST, 1927, **52**, 570; 1931, **56**, 172). The flask is swept out with a rapid stream of carbon dioxide for ten minutes, the liquid is then boiled with carbon dioxide passing for a further 15 minutes, after which it is cooled, diluted and titrated exactly as described (ANALYST, 1931, **56**, 173), the only difference being that no citric acid is added to the diluting water. Trials of the above process with known amounts of tin in the absence of other metals, gave the following results:

Tin taken Grm.	Titration *N*/10 iodine solution c.c.	Tin found Grm.
0·0500	8·40	0·0498
0·0400	6·70	0·0398
0·0300	5·15	0·0306
0·0200	3·35	0·0199
0·0100	1·70	0·0101

SEPARATION FROM LARGE AMOUNTS OF COPPER (*e.g.* DETERMINATION OF TIN IN BRONZE).—The procedure adopted was as follows:—Five grms. of the sample were dissolved in 50 c.c. of dilute nitric acid (sp.gr. 1·2) and 10 c.c. of strong hydrochloric acid, 20 c.c. of the citric acid solution were added and, after making the liquid alkaline with ammonia, the blue colour was just discharged with the potassium cyanide, and 10 c.c. of the latter were added in excess; the ammonium

sulphide and sodium hydrosulphite were then added, and the remainder of the process was carried out as before. Results:

Copper taken Grms.	Tin taken Grm.	Titration c.c.	Tin found Grm.	Tin added Per Cent.	Tin found Per Cent.
5·00	*Blank	0·5 (N/100)	0·0003	—	—
5·00	0·0500	8·50—0·05 (N/10)	0·0502	1·00	1·00
5·00	0·0400	6·65—0·05 (N/10)	0·0392	0·80	0·78
5·00	0·0300	5·05—0·05 (N/10)	0·0297	0·60	0·59
5·00	0·0200	3·40—0·05 (N/10)	0·0199	0·40	0·40
5·00	0·0100	1·65—0·05 (N/10)	0·0095	0·20	0·19
5·00	0·0050	8·8 —0·5 (N/100)	0·0049	0·100	0·098
5·00	0·0040	6·9 —0·5 (N/100)	0·0038	0·080	0·076
5·00	0·0030	5·4 —0·5 (N/100)	0·0029	0·060	0·058
5·00	0·0020	3·9 —0·5 (N/100)	0·0020	0·040	0·040
5·00	0·0010	2·0 —0·5 (N/100)	0·0009	0·020	0·018

Separation from Large Amounts of Copper and Zinc (Determination of Tin in Brass).—In this case the procedure was almost the same, but, on the addition of ammonium sulphide, after decolorisation of the copper, zinc sulphide precipitated; potassium cyanide solution was then added until the zinc sulphide had redissolved, followed by 20 c.c. in excess, an excess of ammonium chloride was added (about 20 grms.), followed by the hydrosulphite, the liquid was boiled, and the determination was finished as before. Results obtained were as follows:

Brass taken Grms.	Tin added Grm.	Titration c.c.	Tin found Grm.	Tin added Per Cent.	Tin found Per Cent.
5·0	*Blank	0·8 (N/100)	—	—	—
5·0	0·050	8·50—0·10 (N/10)	0·0499	1·00	1·00
5·0	0·100	17·00—0·10 (N/10)	0·1003	2·00	2·01
5·0	0·030	5·05—0·10 (N/10)	0·0294	0·60	0·59
5·0	0·010	1·75—0·10 (N/10)	0·0098	0·20	0·20
5·0	0·0050	9·1 —0·8 (N/100)	0·0049	0·100	0·098
5·0	0·0030	5·6 —0·8 (N/100)	0·0028	0·060	0·056
5·0	0·0020	3·9 —0·8 (N/100)	0·0018	0·040	0·036
5·0	0·0010	2·2 —0·8 (N/100)	0·0008	0·020	0·016

* The blank in these two cases represents tin present in the metals used; accordingly, 0·5 c.c. of N/100 and 0·05 c.c. of N/10 solutions, in the case of copper, and 0·8 c.c. of N/100 and 0·10 c.c. of N/10 solutions, in the case of brass, has been deducted from the titration figure.

The case of the determination of tin in brass brings out a point which it is important to bear in mind. Stannous sulphide, whilst insoluble in ammonia and in alkali hydroxides, is apparently not produced by hydrosulphite reduction in presence of the latter, and potassium cyanide is strongly alkaline; it is, therefore, essential that an excess of ammonium salts should be present to eliminate the retarding power of the potassium cyanide used. In the case of copper this excess is furnished by the acid used in dissolving the sample, which is subsequently neutralised with ammonia; in the case of brass, the ammonium salts thus present

are not sufficient, owing to the large excess of cyanide which has to be used, and consequently it was found necessary to add not less than 20 grms. of ammonium chloride. It is always desirable to test the filtrate and washings to ensure complete precipitation; to do this, they are boiled with the addition of a little more hydrosulphite, but in case the ammonium salts have been insufficient, more ammonium chloride should be added as well. It sometimes happens that the decomposition of cyanide caused by boiling with ammonium salts brings the amount present below that required to keep the copper sulphide in solution; therefore, before assuming that a darkening appearing when the filtrate is tested is due to incomplete precipitation, it is well to add a few drops of the cyanide solution, which will redissolve any copper sulphide thus formed, while leaving stannous sulphide untouched.

Separation from Lead.—Attempts were made to separate tin from lead and antimony by this method. The precipitation of lead as metal by hydrosulphite will apparently take place equally well in sodium hydroxide solutions, whilst that of stannous sulphide is inhibited by this reagent. Accordingly, 5-grm. quantities of lead, to which varying amounts of tin had been added, were dissolved in 50 c.c. of citric acid solution (100 grms. dissolved in 200 c.c. of water) and 50 c.c. of dilute nitric acid (sp.gr. 1·2), sodium hydroxide solution (20 per cent.) was added until the precipitate first formed redissolved, then 10 c.c. of saturated potassium cyanide solution (treated with 2 or 3 drops of bromine water), and, finally, sodium hydroxide solution again until the precipitate redissolved, and then 10 c.c. in excess; about 7 grms. of hydrosulphite were added, and the liquid was heated to boiling; it was then cooled and filtered, and the precipitated lead was washed with a mixture of 10 c.c. of saturated potassium cyanide solution, 10 c.c. of sodium hydroxide solution (20 per cent.), 5 grms. of sodium chloride and 2 grms. of sodium hydrosulphite in 200 c.c. To the filtrate were added 20 grms. of ammonium chloride, 5 grms. of hydrosulphite and 10 c.c. of ammonium sulphide; it was heated to boiling, and the tin was determined as before. The following results were obtained:

Lead taken Grms.	Tin added Grm.	Titration c.c.	Tin found Grm.	Tin added Per Cent.	Tin found Per Cent.
5·0	0·1000	16·72 (N/10)	0·0993	2·00	1·99
5·0	0·0700	11·63 (N/10)	0·0691	1·40	1·38
5·0	0·0500	8·26 (N/10)	0·0491	1·00	0·98
5·0	0·0200	3·27 (N/10)	0·0195	0·40	0·39
5·0	0·0100	1·71 (N/10)	0·0101	0·20	0·20

The precipitated lead in each case was tested for tin, with negative results. The above figures seem to show that the method gives a very fair separation of tin from lead.

Attempted Separation from Antimony.—The method used for lead was tried for antimony, but with indifferent success. Only 0·1 grm. of antimony was taken, and varying amounts of tin were added, but the separation was by no means complete, as not only were traces of tin found in the antimony, but antimony was

also found in the stannous sulphide precipitate. The figures obtained for the tin were, however, only slightly low. Results were as follows:

Antimony taken Grm.	Tin added Grm.	Titration c.c.	Tin found Grm.
0·10	0·1000	16·66 (*N*/10)	0·0989
0·10	0·0700	11·63 (*N*/10)	0·0691
0·10	0·0500	8·21 (*N*/10)	0·0488
0·10	0·0200	3·03 (*N*/10)	0·0180
0·10	0·0100	1·61 (*N*/10)	0·0096

SEPARATION OF TIN FROM IRON.—Experiments showed that there is no difficulty in separating tin from large amounts of iron, the iron being first quantitatively converted into ferrocyanide by the action of potassium cyanide and hydrosulphite. The amount of cyanide required, however, is so large that, in view of easy separations by other means, the method did not seem worth following up. In addition to this, the presence of another metal having a ferrocyanide sparingly soluble in alkaline solution (*e.g.* manganese) might cause serious complications.

DETERMINATION OF TIN IN STEEL.—The above considerations made it seem desirable to effect an initial separation from the iron present by means of hydrogen sulphide; trials made on these lines, however, gave very low results, and it soon became apparent that the tin was not being completely precipitated.* Attempts were, therefore, made by the addition of a relatively large amount of another precipitable metal (*e.g.* copper) to obtain complete precipitation; the results obtained, whilst occasionally correct, were generally low; it would seem that tin does not co-precipitate with copper to any large extent. Analogy of the two metals and the difficulty experienced in separating them led to the trial of antimony as co-precipitant, and this gave satisfactory results. Bearing in mind the fact that nearly all steels contain traces of copper, and that the latter metal has a very bad influence on the volumetric determination of tin, the tin was subsequently precipitated as stannous sulphide as described further back; this, of course, involved the precipitation of, at least, the greater part of the antimony, but as shown in a previous paper (Evans, ANALYST, **1931, 56, 174**), antimony in reasonable amount need have no harmful influence on the titration.

Process.—The steel used for these experiments had the following composition: —Carbon, 0·29; silicon, 0·025; manganese, 0·25; nickel, 2·05; and chromium, 2·20 per cent. Samples were dissolved in dilute (1:6) sulphuric acid (for 5 grms. 100 c.c. were used). Varying amounts of tin in solution were added, followed in each case by 0·05 grm. of antimony in solution in dilute (1:1) hydrochloric acid. The mixture was diluted with an equal volume of water, hydrogen sulphide was passed for about 15 minutes, and the flask was allowed to stand for 30 minutes. After this time the precipitated sulphides were filtered off and washed with

* Scherrer (*Bur. of Standards., J. Research,* 1932, **8**, 309) finds the same difficulty where (as above) the hydrogen sulphide is passed into the *ferrous* solution; he avoids it by oxidising all the iron to the ferric state with nitric acid; this involves large amounts of sulphur being precipitated along with the sulphides.

5 per cent. ammonium chloride solution; the funnel having been transferred to the original flask, a mixture of 10 c.c. of sodium hydroxide solution (20 per cent.) and 10 c.c. of hydrogen peroxide was poured through the filter, which was then washed two or three times with hot water. The filter was then transferred to a beaker, broken up with a glass rod, and heated with 50 c.c. of a saturated solution of bromine in dilute hydrochloric acid (1 : 1); the liquid was then filtered through a small filter into the alkaline liquid in the original flask, and the filter was pressed down with a glass rod, and washed with hot water. The united filtrates were decolorised with sulphurous acid, 20 c.c. of citric acid solution (100 grms. dissolved in 200 c.c. of water) were added, followed by an excess of ammonia, 10 c.c. of potassium cyanide solution (saturated), 5 c.c. of ammonium sulphide, 25 c.c. of ammonium chloride solution (20 per cent.), and, finally, 8 grms. of hydrosulphite; the liquid was then boiled for one minute, 1 or 2 grms. more hydrosulphite added, and the precipitated stannous sulphide was allowed to settle, filtered off and determined as usual, 10 c.c. of citric acid and 30 c.c. of potassium iodide solution being used in the diluting solution in the last stage.

The following results were obtained:

Steel taken Grms.	Tin added Grm.	Antimony added Grm.	Titration c.c.	Tin found Grm.	Tin added Per Cent.	Tin found Per Cent.
5·0	Blank	0·05	0·5 (N/100)			
Blank	Blank	0·05	0·3 (N/100)			
5·0	0·0040	0·05	6·8—0·3—0·2=6·3 (N/100)	0·0038	0·080	0·076
5·0	0·0030	0·05	5·4—0·3—0·2=4·9 (N/100)	0·0029	0·060	0·058
5·0	0·0020	0·05	4·1—0·3—0·2=3·6 (N/100)	0·0021	0·040	0·042
5·0	0·0010	0·05	2·2—0·3—0·2=1·7 (N/100)	0·0010	0·020	0·020
20·0	0·0010	0·05	2·7—0·3—0·8=1·6 (N/100)	0·0009	0·0050	0·0045

The significance of the two "blanks" and of the two sets of figures deducted from the titration results is as follows:—The test made on the steel used, without addition of tin, and with the conditions otherwise the same, required 0·5 c.c. of N/100 iodine solution; the test made on the antimony alone without addition of either steel or tin required 0·3 c.c.; the difference between these two figures, 0·2 c.c. N/100 iodine, represents tin present in the sample of steel used as a basis, and therefore, whilst being peculiar to this particular series, had to be deducted from the titration values of those tests which were carried out on 5 grms. of steel; in the case where 20 grms. of steel were used, the 0·2 c.c. had, of course, to be multiplied by 4. The 0·3 c.c., representing tin contained in the antimony solution, is a general reagent blank, and had to be deducted from all the determinations indiscriminately, and, of course, from any that might be carried out with the same antimony solution. With an unknown antimony solution it is necessary to determine the blank.

Recovery of Tin from Organic Acid Solution.—As has been already stated, hydrosulphite methods have not, up to the present, proved amenable for the complete separation of antimony and tin. One of the best of the older processes for this purpose is Clarke's method of precipitating the antimony with hydrogen sulphide, in presence of a large excess of oxalic acid; this process, whilst

excellent so far as antimony is concerned, has the serious drawback that the oxalic acid has to be destroyed before the tin can be recovered. The hydrosulphite process, taking place, as it does, entirely in alkaline solution, is especially adapted for the recovery of tin from this solution. Some trials were made with 0·2 grm. of antimony and varying amounts of tin; after Clarke's separation had been carried out, the filtrate was made alkaline with ammonia, 5 c.c. of saturated potassium cyanide solution were added, and 5 c.c. of ammonium sulphide, followed by about 8 grms. of hydrosulphite. The solution was boiled for 1 minute, 2 or 3 grms. more hydrosulphite were added, and the precipitate was allowed to settle on the steam-bath and then filtered off and the determination was finished as usual. The results were as follows:

Antimony taken Grm.	Tin added Grm.	Titration c.c.	Tin found Grm.	Tin added, Per Cent.	Tin found Per Cent.
0·20	0·010	15·8 (*N*/100)	0·0094	5·0	4·7
0·20	0·008	12·8 (*N*/100)	0·0076	4·0	3·8
0·20	0·006	9·8 (*N*/100)	0·0058	3·0	2·9
0·20	0·004	6·5 (*N*/100)	0·0039	2·00	1·95
0·20	0·002	3·3 (*N*/100)	0·0019	1·00	0·95

A point which emerged during this work was the absolute necessity of working with *hot* concentrated solutions of oxalic acid in carrying out Clarke's separation; on trying it with cold saturated oxalic acid solution less than half of the tin was sometimes recovered. Most text-books, whilst giving correct directions, do not seem to stress this point as it deserves.

The Relative Vitamin *A* and Vitamin *D* Content of Samples of Cod-Liver Oil*

By KATHARINE H. COWARD, D.Sc., F. J. DYER, B.Sc., and BARBARA G. E. MORGAN

For many years the "blue value" of a sample of cod-liver oil (obtained by the action of antimony trichloride upon it) has been accepted as, at least, an approximate measure of the vitamin *A* content of the oil. This would appear to be justified only in so far as an oil with a high blue value has usually been found to have a high vitamin *A* value (as measured biologically), and an oil with no blue value has been found to have no vitamin *A* value. Latterly, however, since the biological method of estimating vitamin *A* has been rendered more accurate, serious doubt has been thrown on the degree of correlation between the blue value of an oil and its true vitamin *A* value.

Moreover, much work has been carried out that shows that (*a*) the blue value of an oil may be decreased by the presence of certain other substances in the oil (Drummond and Hilditch,[1] 1930; Norris and Church,[2] 1930), and (*b*) the blue

* Communication from the Pharmacological Laboratories, Pharmaceutical Society of Great Britain.

colour obtained in this test is due to the absorption bands of two substances, one of which is known to be influenced by certain processes (such as the blowing of ozonised oxygen through the oil), whilst the other is not influenced by these particular processes (Heilbron, Gillam and Morton,[3] 1931). The band which is not thus influenced appears to be associated with the absorption band 328$m\mu$ of the oil—the band whose intensity, so far, has shown the best agreement with the vitamin *A* value of an oil. Even if the vitamin *A* in a particular oil gives rise to a certain "blue value," the "blue value" of the oil itself may be greater or less than that due directly to the vitamin as such. It is not surprising, therefore, that the more accurate measurements of vitamin *A* in oils should fail to agree well with the "blue values" of those oils. The practice of converting a "blue value" into a vitamin *A* value simply by multiplying it by a constant factor is, at least, unsafe. To call the result "biological units" implies the performance of a biological test, which is wholly misleading.

The procedure of multiplying the "blue value" by another constant and calling the result vitamin *D* units is still more unsound. It rests simply on the assumption that if an oil is rich in vitamin *A*, it will be proportionately rich in vitamin *D*. The only evidence of this to be found in the literature is a statement of Drummond and Hilditch[1] (1930) in their report to the Empire Marketing Board on the "Relative Values of Cod Liver Oils from Various Sources." In it, they state that "generally speaking, there is a parallelism between the vitamin *A* and vitamin *D* potencies of the oils, although a few exceptions are to be noted. Thus, the Norwegian oils, L and Q, are of low vitamin *A* value, but relatively good as sources of *D*." Now a general trend in a correlation between two factors is unsafe as a basis for exact comparisons. The figures of Drummond and Hilditch have only to be examined to show how true this statement is. Oils of the same vitamin *A* value have a vitamin *D* value ranging from 100 to 300 units per grm., which is almost the full range of possible vitamin *D* values of samples of cod-liver oil. Similarly, oils with 200 vitamin *D* units per grm. have vitamin *A* values ranging from 100 to 1000 U.S.P. units. Yet, despite the evidence of these figures and the warning clearly stated by the writers in their report, it has been assumed by some that the vitamin *A* and *D* values run parallel to each other, and that both may be measured by the "blue value" of the oil.

Experience of the Pharmacological Laboratories

To prevent this misconception from gaining further acceptance, it seemed advisable to review the results of the estimation of vitamins *A* and *D* in cod-liver oils carried out in these laboratories.

(*a*) Vitamin *D*.—Since February, 1927, estimations of vitamin *D* have been made in terms of a standard of reference (a solution of irradiated ergosterol prepared by the National Institute for Medical Research), which was accepted in August, 1930, by the Medical Research Council of Great Britain (*B.M.J.*, *Lancet*, *Pharm. J.*, Aug. 30, 1930; Analyst, 1930, **55**, 692), and in October, 1931, by the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations (*cf.* Analyst, 1932, 173). Thus, all the samples of cod-liver oil examined in these laboratories for vitamin *D* have been assayed in terms

of the international standard, and the results expressed in international units, the unit being defined as the antirachitic activity contained in 1 mgrm. of the international standard. Many samples of cod-liver oil have been submitted for vitamin *D* tests only, and the "blue values" of some of these were not determined at the time of the biological examination. They could not, therefore, be included in this review. Those that are included had their "blue colour values" determined at the same time as, or within a month of the biological examination. The results are collected in Table I.

TABLE I

Oils with blue value of:—	Vitamin *D* potency of these oils— units per grm.	Average
4 to 5	88, 100, 100, 150	109·5
6 to 7·5	56, 64, 82, 100, 100	80·4
8 to 10	56, 60	58·0
11 to 15	88, 100, 100, 150	109·5
17 to 20	40, 50, 120, 200, 250	132·0
20·5 to 25	100, 110, 180, 180, 210	156·0
28	200	200
34·5	110	110
45	50	50
50	7·5*	7·5*
107·5	100	100

* Did not smell like cod-liver oil, but had actually been sold as such.

It is evident from Table I that some oils may have the same blue value as other oils, but twice, or even six times, the vitamin *D* value. Even if averages of these values are taken, there is no evidence that a higher vitamin *D* value is associated with a higher blue value. In fact, it will be seen that there is not even a trend of the vitamin *D* values to follow the blue values.

(*b*) VITAMIN *A*.—We have made a similar comparison of the results obtained to date of the vitamin *A* content of oils. Many of these results have already been reported in a paper by Coward, Dyer, Morton, and Gaddum[4] (1931). In this paper it was shown that serious discrepancies may exist between the biological values for vitamin *A* and the "blue values" of the oils. Since then, further examinations of oils have been made by the same method, details of which are to be presented in a second paper. In particular, four oils have been examined with increased refinement of technique, which, we think, can leave no doubt as to the unsoundness of relying on the "blue value" of an oil as a measure of its vitamin *A* potency. The results are collected in Table II. The vitamin *A* potency of each oil has been provisionally expressed in units, the unit being the vitamin *A* activity of 1γ (0·001 mgrm.) of the sample of carotene issued by the National Institute for Medical Research in December, 1930, to certain laboratories for investigation of the possibility of adopting carotene as a standard of reference for vitamin *A*. It is unlikely that the standard preparation of carotene, when issued, will differ materially from the one used in these investigations.

TABLE II

Oil	Colour value of oil (*a*)	Vitamin *A* potency of these oils (*b*)	Colour value relative to oil 1 (=100) (*c*)	Vitamin *A* potency relative to oil 1 (=100) (*d*)
1	4·1	1564	100	100
2	4·4	1568	107	100
3	7·6	3098	185	198
4	9·0	3140	220	201
5	10·2	4916	249	314
6	10·8	2596	263	166
7	11·6	2000	283	121
8	15·2	3510	371	225
9	17·4	2440	424	156
10	20·6	5800	500	352
11	28	3054	683	195
12	86	12546	2098	802
13	305	31246	7439	1998

The figures in Table II demonstrate the *trend* of the vitamin *A* value to follow the colour value, but a comparison of the figures of columns (*c*) and (*d*) shows the serious discrepancy that may occur between the two values for any one oil. A statistical examination of the accuracy of our biological test for vitamin *A* shows that, by the use of ten animals for a test of one dose of a substance, the result will be 21 times out of 22 between 60 and 160 per cent. of the true value. For each test reported in Table II, never less than nine, and often more than ten rats, were used. It is probable, therefore, that the colour values of oils 1, 2, 3, 4, and 5, and possibly 8 and 10, may be said to agree with the biological values. It is evident, however, that in the rest (6 out of 13 samples) the blue values lie well outside the range of the possible biological values. The discrepancies between the blue values and the biological values of these oils must be regarded as serious.

Four other oils have been examined within the last six months, each time in comparison with the standard oil. That is, a fresh test of the standard was made at the same time as the test of each of the four samples. Moreover, each comparison was made by using equal numbers of rats from the same litters for the test sample and for the standard. The values obtained for these four samples are collected in Table III.

TABLE III

Oil	Colour value of oil	Vitamin *A* potency of oil	Colour value relative to oil 1 (=100)	Vitamin *A* potency relative to oil 1 (=100)
1	17·1	11400	100	100
2	19·6	8800	114	77
3	21·4	3000	125	26
4	23·0	6280	135	55

It is of interest to note that the "colour value" of the oil which we have used as a standard of reference in all this work has changed only very slightly during three years. The oil has been kept in the dark at room temperature for two years, and in cold store for the last twelve months.

The results in Table III show even wider discrepancies between blue values and biological values than do those in Table II. One oil with a blue value of 125 per cent. of that of another oil, has a biological value only 26 per cent. of that of the second oil. The oils do not even demonstrate a trend of a high biological value to be associated with a high blue value.

SUMMARY.—The examination of 30 samples of cod-liver oil shows that the "blue colour value" of the oil is no indication of its vitamin *D* potency.

The examination of 17 samples of cod-liver oil shows, on the whole, a definite trend of a high blue value to be associated with a high vitamin *A* value, but it is possible for oils of the same colour value to have vitamin values differing by as much as 400 per cent. Thus, the blue colour value of an oil cannot be considered a measure of its vitamin *A* potency. Moreover, the vitamin *D* values of different samples of cod-liver oil are not proportional to the vitamin *A* values.

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The Nitro-Chromic Acid Reaction for the Detection of Primary and Secondary Alcohols, with Special Reference to Saccharides

BY WILLIAM ROBERT FEARON, SC.D., F.I.C., AND DAVID MICHAEL MITCHELL, B.A.

WHILE it has been known for many years that solutions of chromic acid are readily reduced by compounds of the alcohol type, the scope and conditions of the reaction are not yet fully investigated. When a sugar solution of about 1 per cent. concentration is treated with an equal volume of concentrated nitric acid and a few drops of a 5 per cent. solution of potassium dichromate, a blue colour develops in less than a minute in the cold solution. This reaction, which we observed for the first time recently, is given by all saccharides and other compounds containing a primary or a secondary alcohol group. On reviewing the literature, it was found to be similar to a reaction described by Agulhon (*Bull. Soc. Chim.*, 1911, **9**, 881), but it is capable of a much greater degree of specificity than he appears to have realised.

SCOPE OF THE REACTION.—According to Agulhon, the reaction is given by all aldehydes, by all primary, secondary, and tertiary alcohols, and by all aliphatic

compounds containing aldehyde or alcohol groups. Aliphatic ketones react also, but require a longer time. During our independent investigation of the reaction it appeared probable that the test can be applied so as to distinguish primary and secondary alcohols from tertiary alcohols, a conclusion in accordance with what is known regarding the relative stability towards oxidation exhibited by each of these three classes of compounds. We may use a reagent consisting of 5 per cent. potassium dichromate in nitric acid, diluted 1 : 2, and add 5 c.c. of the reagent to 1 c.c. of the solution to be tested; or we may employ a 5 per cent. solution of potassium chromate instead of the original dichromate. This modification we have studied under the name of the nitro-chromic acid test.

THE NITRO-CHROMIC ACID TEST.—Five drops of 5 per cent. potassium chromate solution are added to 5 c.c. of nitric acid previously diluted in the proportion of 1 to 2 with water, and cooled. Then 0·1 to 1·0 c.c. of the solution to be tested is added, and the mixture is shaken. A positive result is shown by the development of a blue or blue-violet colour within 1 to 5 minutes, depending on the dilution. The test is positive with all of the familiar primary and secondary alcohols, with all saccharides, with formaldehyde, and with hydroxy acids, such as lactic and tartaric acid. The test is negative with tertiary alcohols, aldehydes other than formaldehyde, aliphatic ketones, oxalic acid, citric acid, and the acids of the acetic series, amino acids and amino compounds, such as urea, polymeric compounds, such as paraformaldehyde, metaldehyde, and (under restricted conditions) the polysaccharides. Phenols do not give the blue colour, although they interact variously with the nitric acid.

Nitrites, peroxides, and hypo-halites also develop a blue colour with the reagent—a reaction which is quite distinct from the ultramarine-blue colour of the familiar peroxide test for chromium salts.

Oxalates react anomalously. No blue colour appears within the first few minutes, but when the mixture has been kept for several hours a dichroic purple colour develops. Apart from these exceptions, the test appears to be specific for the groups $-CH_2.OH$ and $=CH.OH$, the response of formaldehyde being attributable to enolisation.

APPLICATION OF THE TEST.—1. *Distinction between Primary, Secondary and Tertiary Alcohols.*—The test is sufficiently specific not to be given when a drop of a pure tertiary alcohol is added to 5 c.c. of the cold reagent, although primary and secondary alcohols react readily in 0·1 to 1·0 per cent. concentration. The test may also be applied to show the presence of impurities in specimens of tertiary alcohols.

2. *Distinction between Hydroxy and Non-hydroxy Acids and Differentiation of Hydroxy Acids.*—The test will distinguish rapidly between tartaric and citric acids, the former reacting positively.

3. *Distinction between Carbohydrates and other Bio-organic Compounds such as Fats and Proteins.* Carbohydrates, unlike fats and proteins, give a positive reaction. Normal urine does not give the reaction; nor does blood serum, as the sugar content is below the critical limit of the test.

4. *Distinction between Saccharides and Polysaccharides.*—Insoluble polysaccharides, such as cellulose, do not give the reaction; soluble polysaccharides, such as starch, inulin and dextrins, give the reaction in accordance with their instability towards the acid in the reagent. Thus, by reducing the concentration of nitric acid, it is possible to obtain a mixture which reacts rapidly with saccharides and not with polysaccharides, but this is partly determined by the concentration of carbohydrate. With nitric acid diluted with water (1:4), a 1 per cent. solution of glucose or maltose gives the blue coloration within 5 minutes, whereas a 1 per cent. solution of starch may remain for several hours without reducing the chromic reagent. The observation is of interest on account of the hypothesis advanced by Haworth (*The Constitution of the Sugars*, 1929), that the polysaccharide is composed of conjugated saccharide units, joined by co-valent links. The relative slowness of reaction with the chromic reagent indicates that the $-CH.OH$ groups in the polysaccharide complex are masked in some manner.

DELICACY OF THE TEST.—The time taken for the development of the blue colour increases greatly with the dilution of the alcohol. Taking 1 minute as the time-limit, a positive result is obtained with primary alcohols in 0·1 per cent. concentration; with secondary alcohols in 0·5 per cent. concentration; and with saccharides in 1·0 per cent. concentration. Extending the time-limit to 1 hour, a positive result may be obtained with ethyl alcohol in 0·01 per cent. concentration; and with glucose in 0·08 per cent. concentration.

MECHANISM OF THE TEST.—A discussion of the mechanism is outside the scope of the present paper. That the colour of blue pigment produced differs from the ultramarine-blue coloration formed in the peroxide test for chromates is shown by its insolubility in ether, and by the fact that the peroxide pigment is bleached by strong acids. The pigment itself is, presumably, the anhydride of nitrous acid formed under conditions comparable with those of the Debus reaction for the preparation of glyoxylic acid by the oxidation of alcohol with excess of nitric acid. The chromium salt determines the specificity of the test. When a dichromate is used, and introduced after the other reactants have been mixed, or is added in excess, as in the original Agulhon reaction, the test loses its specificity, owing, presumably, to the action of the chromic anhydride.

DEPARTMENT OF PHYSIOLOGY,
TRINITY COLLEGE, DUBLIN.

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.

NITRATES IN MILK AS EVIDENCE OF ADDED WATER

As recorded in the Annual Report of the County Analyst for Somerset for 1931 (ANALYST, 1932, 247), one sample of milk contained nitrates but showed no evidence of added water. My attention has been called by Mr. H. H. Bagnall, B.Sc., F.I.C., City Analyst of Birmingham, to the practice, on the part of milk producers, of adding saltpetre to milk to remove the taste and smell given by feeding on turnips, and enquiry showed that the producer of this milk was in the habit of adding a small amount of saltpetre in the summer months to keep the milk sweet. The sample was collected in August.

The above instance shows the importance of making inquiries, and also shows that accidental contamination with nitrates did not occur with this sample; it did not occur with any of the other 469 samples, so that it is an extremely unlikely contingency (*cf.* G. D. Elsdon and J. A. Sutcliffe, ANALYST, 1913, **38**, 451; G. D. Elsdon and P. Smith, ANALYST, 1922, **47**, 18; and G. D. Elsdon, ANALYST, 1923, **48**, 115).

COUNTY LABORATORY, D. R. WOOD.
WESTON-SUPER-MARE, SOMERSET.

FLUORESCENCE OF MILK AND BUTTER IN ULTRA-VIOLET LIGHT

1. Our experience in these laboratories with Kelvin, Bottomley and Baird's quartz lamps during the past twelve months has shown that the fresh milk of the cow, goat or sheep exhibits a canary-yellow fluorescence, but we are unable to agree with Popp (ANALYST, 1926, **51**, 540) that this is an attribute of the fat.

2. Skim-milk whey retains much of the original fluorescence, but the separated cream is of a much paler yellow than the whole milk. This point is strikingly demonstrated in the Gerber butyrometer, where the column of fat is devoid of the yellow fluorescence, whilst the acid liquid, which is dark brown in daylight, is bright canary-yellow in ultra-violet light.

3. If fresh milk, either skimmed or whole, is kept in a test tube at the ordinary temperature for a day or more, the yellow fluorescence gradually gives place to a bluish colour, developing from the bottom upwards. If, however, the milk is boiled, or if formalin is added, this change does not take place.

4. If this "blue" milk is now shaken in the tube the yellow fluorescence at once returns, but gives place to blue again on standing for an hour or so. If, however, air is removed by means of a pump from the tube containing the regenerated yellow milk, the change to blue is very rapid.

5. A sample of curd cheese, which also exhibited a superficial bright yellow fluorescence, showed blue fluorescence, quickly changing back to yellow on exposure of a freshly-cut surface. This cheese, when repeatedly washed, lost most of its yellow fluorescence, which was transferred to the washing water.

6. Control experiments in an atmosphere of carbon dioxide or of nitrogen have shown that oxygen is the active agent in the regeneration of the yellow

fluorescence. Its destruction would appear to be due to an agent similar to that which decolorises methylene blue in the "reductase test," and in this connection it has been found that the methylene blue will also regain its colour on aeration.

7. The colour of milk-fat, including ordinary churned butter and native samneh (rendered butter-fat), in ultra-violet light has shown variations between creamy white and yellow, which are often, but not always, accentuations of the shades of colour observed in daylight.

8. Samples of coconut fat have shown an intense blue fluorescence, and in experimental tests as little as 5 per cent. of this fat was found to affect the colour of butter-fat, although from 10 to 20 per cent. was required to give a definite indication of adulteration when the exact tint of the original pure butter was unknown.

9. As a result of the examination of 959 samples, most of which were native samneh, we find that a bluish tint is a fairly reliable indication of adulteration, whilst the absence of any suggestion of yellow is to be viewed with suspicion. Actually, of 89 adulterated samples, 86 exhibited some degree of bluish fluorescence, whilst of the 870 genuine samples 99 per cent. had a fluorescence ranging from creamy white to yellow.

10. Samples of freshly-rendered butchers' fat from the cow, sheep and goat could not be placed definitely outside the colour range of butter, but, after being kept for a month, they all developed a dirty blue fluorescence, although, apparently, they were still in good condition.

11. Artificial colouring matter may mask the fluorescence, but the coloured fats so far met with have yielded to treatment with boiling water and charcoal (0·3 grm. of charcoal to 10 grms. of fat). The charcoal may impart a blue fluorescence to the water, but this does not interfere with the colour of the fat.

12. In carrying out the fluorescence test we use, for comparison, standard samples of adulterated and pure butter-fat. In doubtful cases differences are often accentuated if the fats for comparison are spotted in a semi-solid state, side by side, on a sheet of paper.

13. There are many avenues for further investigation, and there may be disturbing factors not yet encountered, but we have so far found the test to be of considerable practical value; more so, perhaps, than any other single routine test, with the exception of the determination of the volatile fatty acids. Under conditions obtaining here, for example, the taking of large numbers of unofficial samples is often useful as a means of indicating the vendors who require further attention, and, in such cases, a rapid test of this kind is invaluable, so long as its limitations are recognised.

G. W. Baker.
S. Taubes.

Government Central Laboratories,
Department of Health, Jerusalem.

THE SOLUBILITY OF URANYL ZINC SODIUM ACETATE IN ALCOHOL OF DIFFERENT STRENGTHS

For the determination of sodium as uranyl zinc sodium acetate, and also in the colorimetric determination of sodium, a knowledge of the solubility of the triple salt in alcohol of different strengths is important.

The interference of alcohol in the microchemical method of comparing the colour developed from an amount of triple salt equivalent to 0·1 mgrm. of sodium, in water, with that produced from the same amount of salt in alcohol of different

strengths, is shown in the following table. The standard was set at 30 mm. in the colorimeter, and the average of four readings was taken.

Alcohol. per cent. by vol.	Average reading. mm.	Average error. Per Cent.
0	30	0
10	28·6	4·7
20	27·0	10·0
30	25·8	14·0
40	23·4	22·0
50	20·8	30·7

The solubility of the triple salt was determined by evaporating to dryness 10 c.c. of the saturated solution. The results at 25° C. are given in the following table:

Concentration.	Solubility in 100 c.c. Grm.
Absolute alcohol	0·132
96 per cent. by vol.	0·042
90 ,, ,, ,, ,, ...	0·062
80 ,, ,, ,, ,, ...	0·119
70 ,, ,, ,, ,, ...	0·194
60 ,, ,, ,, ,, ...	0·316
50 ,, ,, ,, ,, ...	0·967

UNIVERSITY OF STELLENBOSCH,
S. AFRICA.

G. W. B. VAN DER LINGEN.

THE COMPOSITION OF LINSEED OIL

IN a paper by N. E. Cocchinaras on "The Composition of Linseed Oil" in the April number of THE ANALYST, p. 234, appeared the statement, attributed to me, that linseed oil contains 4 per cent. of oleic acid, 20 per cent. of palmitic acid, and 51·7 per cent. of stearic acid; moreover, the reference should be *J. Soc. Chem. Ind.*, 1913, **32**, 1091, and not ANALYST, 1914, **39**, 70.

If the author had read my paper he would have found that the percentages of stearic and palmitic acids were 4·1 and 1·3, respectively. The saturated acids obtained from the lead salts of Calcutta oil were found to be 6 per cent., with melting-point of 53–55° C. In the examination of oil from British-grown linseed (Eyre and Morrell, *Publications of the British Flax and Hemp Growers' Society*, No. VI, 1918) the percentage of saturated glycerides in English-grown linseed was given as 4 per cent. Unpublished results show that the oil obtained from seeds of different stages of ripeness from English-grown linseed (special variety of La Plata seed produced at Wye) had the following characteristics:

BRITISH-GROWN LINSEED FROM WYE (KENT) SUPPLIED BY DR. EYRE

	Unripe seed	Seed ripened on the stalk	Seed fully ripened before picking	Calcutta oil
Percentage yield of oil ..	27·8	33·3	34·0	—
Sp.gr. at 15°/15° C. ..	0·9337	0·9320	0·9317	0·9329
Acidity, per cent.	1·98	—	0·568	1·54
$n_D^{14°\text{-}15°}$	1·4819	1·4847	1·4849	1·4830
Saponification value ..	190·5	—	189–191	192–193·5
Iodine value (Wijs), 1½ hours	185–186	190–194·5	188	189–190
,, ,, 24 ,,	189	193	196	191·4
Percentage of saturated acids	3·4	3·6	4·5	7·56

The yield of the oil increases with ripening, with slight increase in the iodine value, and also in the percentage of saturated acids. A sample of Calcutta oil contained 7·56 per cent. of saturated acids. As the iodine values of oils from different countries vary, so do the percentages of saturated acids.

R. S. MORRELL.

TOR LODGE, TETTENHALL WOOD,
WOLVERHAMPTON.

Official Appointment

THE Minister of Health has approved the following appointment:

ALAN WEST STEWART, D.Sc., A.I.C., as Public Analyst for the Boroughs of Newbury and Windsor (New), in place of Sir W. R. Smith (deceased), (May 24th, 1932).

Ninth Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods

THE DETERMINATION OF CARVONE AND MENTHONE

THE investigations of the Essential Oil Sub-Committee on the determination of ketones in essential oils have shown that, in the case of carvone and menthone, the hydroxylamine method gives results which approximate very closely to the actual content. The oxime formation takes place slowly in the cold, but is accelerated by heat. It proceeds most rapidly when the liberated acid is neutralised at frequent intervals. It has been found necessary, in order to obtain accurate results, to standardise the conditions very carefully. Particularly is it essential to allow the reaction to proceed for a definite time only, as experiments appear to indicate that a secondary reaction takes place very slowly and continues for some hours.

The Sub-Committee recommends the following method for the determination of carvone in caraway oil, dill oil and spearmint oil, and for menthone in peppermint oil.

The following solutions are required:

Indicator Solution.—A 0·2 per cent. solution of dimethyl yellow (*p*-dimethylaminoazobenzene) in 90 per cent. alcohol.

N Alcoholic Potash.—Prepared with 90 per cent. (by volume) alcohol and standardised against *N* hydrochloric acid, using dimethyl yellow as indicator and running the alkali *into* the acid until the full yellow colour is obtained.

N Hydroxylamine Hydrochloride Reagent.—Dissolve 6·95 grms. of pure hydroxylamine hydrochloride in 95 c.c. of 90 per cent. (by volume) alcohol, add 0·4 c.c. of dimethyl yellow solution, and adjust to the full yellow colour of the indicator with *N* alcoholic potash, and make up to 100 c.c. with 90 per cent. (by volume) alcohol.

The full yellow colour of the indicator may be defined as that colour which is not changed by the further addition of alkali.

The alcohol used must be free from aldehydes and ketones.

METHOD OF DETERMINATION.—Weigh out exactly into a stoppered tube (approximately 150 mm. long by 25 mm. in diameter) about 1·5 grms. of caraway, dill or spearmint oil, or 3 grms. of peppermint oil; add 20 c.c. of the *N* hydroxylamine hydrochloride reagent, and titrate with *N* alcoholic potash until the red colour changes to yellow. Place the tube in a water-bath at 75° to 80° C.,* and neutralise the liberated acid with *N* alcoholic potash at five-minute intervals; at the expiration of 40 minutes complete the titration to the full yellow colour of the indicator and note the reading of the burette.

Two determinations should be carried out side by side, using two burettes, and the one first completed, *plus* a slight excess of alcoholic potash (0·5 c.c.), should be used as a colour standard for the end-point of the duplicate. The percentage should be calculated from the duplicate determination.

The number of c.c. of *N* alcoholic potash required, multiplied by the correcting factor 1·008, by the factor 0·150 for carvone or 0·154 for menthone, and by 100, and divided by the weight of oil taken will give the percentage (by weight) of the ketones calculated as carvone or as menthone.

The correcting factor is necessary, owing to the fact that the end-point of the titration occurs at a *p*H different from that of normal hydroxylamine hydrochloride.

Determinations made by members of the Sub-Committee lead us to the opinion that the maximum variation with this method should not exceed ±1 per cent. The following tables show the results obtained by members of the Sub-Committee on samples circulated for collective testing:

PERCENTAGE OF MENTHONE IN PEPPERMINT OIL

Sub-Committee Member	Raw American oil	Japanese oil	Saponified and distilled American oil
No. 1.	23·7	33·4	22·1
	23·3		21·8
No. 2.	21·6	32·5	21·1
No. 3.			21·8
			21·1
No. 4.	22·5	32·3	
	22·4	32·1	
	22·3	32·7	
	22·3	32·2	
No. 5.	22·3	31·9	22·1
	22·3		22·2
	21·9		
	21·9		
No. 6.		31·6	23·4
			23·3
No. 7.			21·8
			21·7
No. 8.	22·0	31·8	22·1
	21·9	32·6	
	22·2	31·8	
Variation	21·6 to 23·7	31·6 to 33·4	21·1 to 23·4
Mean	22·3	32·3	22·0

* A beaker of water standing on a boiling water-bath provides a suitable water-bath at a temperature of 75° to 80° C.

PERCENTAGE OF *d*-CARVONE

Sub-Committee Member	Purified *d*-carvone	*d*-Carvone mixture containing 55·45 per cent. of *d*-carvone	Caraway oil	
No. 1.	98·9	54·7	57·9	
	99·0	55·1		
No. 2.	99·3	55·6	57·0	
			57·2	
No. 3.			57·1	
		55·8	57·1	
			57·5	
No. 4.	99·2	54·9	57·2	58·1
	99·7	55·6	57·3	58·2
	99·8	55·1	57·4	58·7
	99·7	56·2	57·4	
No. 5.	99·8	55·3	57·6	58·4
	99·9	55·7	57·6	58·5
	100·3	55·7	58·0	58·7
	99·9	55·7	58·2	58·9
	99·9		58·4	
No. 6.	99·9	56·0	58·2	
	100·4	56·4	58·6	
No. 7.	99·5	54·7	59·0	
	99·7	54·5		
No. 8.	99·8	55·5	58·0	
	99·9	55·8		
No. 9.	98·3			
	99·3	54·5		
	98·7			
	100·3			
No. 10.	98·7			
	99·4			
Variation	98·3 to 100·4	54·5 to 56·4	57·0 to 59·0	
Mean	99·55	55·4	57·9	

PERCENTAGE OF *l*-CARVONE

Sub-Committee Member	*l*-Carvone mixture containing 52·1 per cent. of purified *l*-carvone	Spearmint oil
No. 1.	53·4	64·0
		64·5
No. 2.	53·1	
No. 3.		62·5
		62·6
No. 4.	53·3	64·9
	53·1	
	53·5	
	53·5	
No. 5.	52·2	
	51·6	
No. 6.	51·7	65·0

PERCENTAGE OF *l*-CARVONE—*continued*

Sub-Committee Member	*l*-Carvone mixture containing 52·1 per cent. of purified *l*-carvone	Spearmint oil
No. 7.	52·1	64·2
	52·5	65·0
	52·2	64·6
	52·8	
Variation	51·6 to 53·5	62·5 to 65·0
Mean	52·7	64·1

(*Signed*),

John Allan (Chairman), C. T. Bennett, S. W. Bradley, E. Theodore Brewis, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, C. Edward Sage, W. H. Simmons, T. Tusting Cocking (Hon. Sec.).

May 1932.

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.

POISONING BY CASTOR SEED

LIABILITY OF PERSON DELIVERING A DANGEROUS ARTICLE

J. TAYLOR & SONS, LTD., *v.* UNION-CASTLE MAIL STEAMSHIP CO., LTD.

IN this action, which was decided on February 17th, 1932, a firm of forage merchants sued the defendants for alleged negligence, claiming £430 damages. In September, 1930, a steamship belonging to the defendants arrived in London with a cargo of maize and other grain, coffee and castor seeds, from Mombasa. The castor seed was shipped with a notice in red ink to the effect that it must be kept separate from the other cargo. On arrival, the Port Authority swept up the grain left on the floor of the hold and divided it *pro rata* among the different holders of bills of lading.

The defendants gave a delivery order to a firm holding a bill of lading for 3584 bags of maize, and this firm sold to the plaintiffs 15 bags, which were, in fact, part of the bags of loose collected cargo, and the plaintiffs mixed these with other grain in the ordinary course of business. A parcel was then sold to a customer, who fed his horses on the grain, with the result that 6 died and 22 were made ill, owing to castor poisoning. It was proved that the grain contained 0·22 per cent. of castor seed, and the plaintiffs settled the claim of their customer for £430, which they now endeavoured to recover from the defendants.

Mr. Justice MacKinnon, in giving judgment for the defendants, said that the extent of the obligation of a person who delivered a dangerous article, to give warning of its nature, must vary with his occupation; for example, it would be higher in the case of a chemist selling a dangerous article than in the case of a

layman. The question must be whether the person delivering the article knew, or, as a reasonable man, ought to have known, that it was dangerous. Here the defendants were not dealers in grain and experts in that particular trade, but were shipowners carrying goods of every possible description.

With regard to the degree of general knowledge of the danger of castor beans, he might say that until the hearing of this case he, himself, knew nothing of that danger; and the evidence had satisfied him that the knowledge was not widely spread. He thought, therefore, that it would be wrong to hold shipowners liable for not warning forage dealers, who might reasonably be supposed to have expert knowledge themselves.

POTTED MEAT PASTE SOLD AS POTTED BEEF

On May 2nd, a manufacturer of potted meat pastes was summoned at Sheffield Police Court for having sold, by the hands of an agent, to a tradesman an article described as "potted beef," but containing 3·9 per cent. of anhydrous starch. There were also summonses against the agent and the tradesman for selling potted beef which contained 4·6 per cent. of anhydrous starch and 71·5 per cent. of water.

The inspector who bought the samples stated that three years ago circulars were sent to the manufacturers of potted beef in Sheffield, advising them that starch should not be an ingredient of potted meat, and also that there should not be more than 70 per cent. of water in potted beef.

Mr. John Evans, F.I.C., Public Analyst for Sheffield, said that starch was a foreign substance in potted meat. There was no legal standard for the amount of water in potted beef, but anything over 70 per cent. was exceptional. He would have taken no exception to the sample being sold as "potted meat paste."

The works-manager of a firm manufacturing various grades of potted beef said that in the best quality they tried to keep the amount of water as near 50 per cent. as possible, and in the cheapest quality it was 65 per cent. They did not introduce starch.

The solicitor for the defence pleaded "guilty" in the case of the tradesman, since the product had been labelled "potted meat" after it had been supplied to him. But the difference between "potted beef" and "potted beef paste" had not been explained to him.

The manufacturer stated that, in the preparation of the paste, 2 lbs. of biscuits were used with 60 lbs. of meat, and that all his wares were described as "potted meat paste."

The magistrates said that they gave the benefit of an element of doubt to the manufacturer and his agent, and would dismiss the cases. The tradesman was fined £5.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Buckwheat Milling and its By-Products. M. R. Coe. (*U.S. Dept. of Agric., Circular No.* 190.)—Buckwheat, *Fagopyrum esculentum*, is milled for flour and groats, and the shorts or middlings, which make up the portion of the grain immediately inside the hull, after separation from the flour, are used as feeding stuffs for cattle. The middlings are a valuable food, containing the oily covering

of the grain and germ, but vitamins *A* and *D* are absent, or present only in small quantities. Too large a proportion of hull must not be present in feeding stuffs, and these hulls are usually burned, although sometimes used as packing material.

The following are typical compositions of buckwheat grain and its products:

	Water Per Cent.	Ash Per Cent.	Fat Per Cent.	Protein Per Cent.	Fibre Per Cent.	Nitrogen-free extract Per Cent.
Buckwheat grain—						
Japanese whole grain ..	10·05	1·71	2·36	10·69	11·37	63·82
Silverhull whole grain ..	10·01	1·81	2·43	11·81	9·92	64·02
Tartary whole grain ..	11·06	1·64	2·32	10·19	15·21	59·58
Buckwheat flour—						
Very light	12·65	0·61	0·05	4·73	0·39	81·12
Light	13·15	1·17	1·29	7·19	0·59	76·61
Medium	12·06	1·37	1·85	9·75	0·96	74·01
Dark	11·67	1·21	1·82	8·94	1·04	75·32
Very dark	13·94	2·21	3·33	15·94	1·21	63·37
Buckwheat hulls—						
Japanese	6·36	2·01	0·76	2·89	49·43	38·55
Silverhull	6·41	1·78	0·53	3·06	52·09	36·13
Tartary	7·85	1·33	0·31	1·93	54·95	33·63

The ash of buckwheat contained: From (1) United States; (2) Mean of Wolff's analyses; K_2O, 35·15, 23·07; Na_2O, 2·26, 6·12; CaO, 6·62, 4·42; MgO, 20·55, 12·42; Fe_2O_3, 1·68, 1·74; P_2O_5, 24·09, 48·67; SO_3, 3·59, 2·11; Cl, 0·67, 1·30; SiO_2, 5·54, 0·23 per cent. D. G. H.

Corrosion of Metals by Milk. H. A. Trebler, W. A. Wesley and F. L. LaQue. (*Ind. Eng. Chem.*, 1932, **24**, 339–350.)—The corrosive action of sweet milk on nickel, copper, nickel-silver, an experimental chromium nickel alloy, and a chromium nickel iron alloy has been investigated. Nickel was found to be only slightly corroded during normal pasteurisation, and the normal increase of corrosion on rise of temperature is prevented by formation of a protective film on the nickel, helped by supersaturation with air and high velocity of the milk. During cooling, the film is not present, and corrosion is appreciable during the first stages, decreasing as the temperature falls, and depending on the usual factors. Supersaturation of the milk with air and high velocity may then operate in the opposite way. Nickel is regarded as suitable for conveying and storing milk at temperatures not above 18° C.; but it should not be used in contact with milk cooling in the range from 63° to 18° C. The addition of sufficient chromium (12 to 15 per cent.) gives an alloy resistant under all conditions to corrosion, and the limited number of tests made on the chromium nickel iron alloy (18 : 8 : 74) indicated that it also would be suitable for milk plants. There was no material film formation on copper, and there is risk of corrosion of copper or nickel-silver in the final stages of heating and the first stages of cooling of milk. Galvanic corrosion was found to be negligible. D. G. H.

Investigation of the Degree of Heating of Milk. Orla-Jensen. (*Z. Unters. Lebensm.*, 1932, **63**, 300–308.)—In the author's "creamometric" method (*Lait*, 1929, **9**, Nos. 86–90) the sample is heated for 5 minutes at 50° C., and 5 c.c.

of milk, plus 5 c.c. of water, and 10 c.c. of undiluted milk are placed in suitable (Höyberg or Gerber) cream-butyrometer tubes, and the thickness of the layer of cream is read in each case after 2 hours at 12 to 15° C. Addition of a colouring matter (*e.g.* the Storch reagent) gives a well-defined layer. The agglutinating powers of milk are weakened by heating, and cream-formation is, therefore, delayed. The ratio (*A*), 2 × thickness of cream in dilute milk/thickness in undiluted milk, should exceed 1 for raw milk, and is less than 1 for milk pasteurised at a low temperature. In certain cases (*e.g.* where the undiluted milk gives only a thin layer of cream) the fat content of the undiluted milk is taken as the denominator. This gives a ratio (*C*) which is 3·9 to 10 (mean 8·3) for raw milk, 0·1 to 3·7 (mean 1·3) for permanently-pasteurised milk, and 0 to 0·3 for milk treated by the Stassan process (momentary heating in a thin layer at 75° C.). Full data, tabulated for 30 samples, show that with milk for children (3·9 per cent. of fat), *A* and *C* are reduced, respectively, from 2·5 and 7·4 for unheated milk, to 1·3 and 4·6 after 15 seconds at 70° C., and to zero after 15 seconds at 78° to 80° C.; corresponding figures for full-milk (fat 3·75 per cent.) are 2·1 and 7·7 (raw), 1·5 and 5·3 (70° C.), 0 (76° to 80° C.). The suitability of other methods proposed as indications of the various degrees of heating of milk is discussed. In particular, estimation of amylolytic power, which is destroyed after 0·5 to 1 hour at 53° C., is a suitable indicator of low-temperature pasteurisation; active amylase in such milk may be due to starch-fermenting streptococci in mastitis milk. Since iodine is held by fat and casein, it is preferable in this test to take 10 c.c. of the whey produced from 40 c.c. of milk after 1 hour at 40° C. in the presence of 1 c.c. of 0·25 *N* hydrochloric acid, and to add 5 drops each of a 5 per cent. solution of potassium iodide and 0·1 per cent. hydrogen peroxide; experiments should be made by the author's method (*loc. cit.*), with the use of 3, 5, 7, or 9 drops of 2 per cent. starch solution. J. G.

Gas Storage of Pork and Bacon. Part I. Preliminary Experiments. E. H. Callow. (*J. Soc. Chem. Ind.*, 1932, **51**, 116–119T.)—Pieces of pork and of mild-cured green bacon, weighing 1 lb., were hung in large vacuum desiccators, containing, at different temperatures, pure or commercial nitrogen, pure or commercial carbon dioxide, or air. At 0° C., pork stored in commercial carbon dioxide was in perfect condition after 2 months, and after 70 days tasted better than fresh pork, and there was practically no loss in weight. In air the meat was overgrown with micro-organisms after 17 days, and in nitrogen, although growth of aerobic organisms was prevented, the development of anaerobic organisms was encouraged, so that this gas is useless for this purpose. For mild-cured green bacon nitrogen was found to be nearly as good as carbon dioxide; the storage life was more than doubled at 5° C., and the colour was brighter than that of bacon stored in air, owing to the apparent stability of nitrosohaemoglobin (to which bacon owes its pink colour) in the absence of oxygen. Carbon dioxide had a marked inhibiting effect on the growth of the micro-organisms obtained from pork suffering from aerobic and anaerobic spoilage. Commercial carbon dioxide prevented growth more effectively than nitrogen. At — 1° C. no growth appeared in pure carbon dioxide in 50 days, but it appeared in 25 days in commercial carbon dioxide and in nitrogen (pure and commercial), and in air it appeared in 4 days. D. G. H.

Fruit Juice Rich in Tannin as a Sensitive Reagent for Pectin. C. Griebel. (*Z. Unters. Lebensm.*, 1932, **63**, 291–300.)—The reagent is best prepared from "speierling" (*Pyrus domestica*), but field pear (*P. communis*), service berry, sloe, cornelian cherry, lotus plum, and other fruits may also be used. The ripe fruit is peeled rapidly with a brass knife, and the juice is removed by pressure, boiled, and filtered while hot. As a reagent it is then stable for 2 or more years so long as it is stored in a filled bottle with a narrow neck, and is covered with a layer of toluene 0·5 cm. deep to prevent access of air, and, consequently, fermentation. If it develops a cloudiness it should be diluted with twice its volume of water and, after 12 hours in the ice-chest, it should again be filtered. For the test, 0·2 c.c. is added in small drops to 1 c.c. of the sample in a small test-tube, when 0·1 per cent. of pectin shows a haze developing into a precipitate, whilst 0·01 per cent. appears as an opalescence (no precipitate). By the use of the technique of Uhlenhut's precipitation test, 1γ of pectin is detectable in 0·5 c.c. of liquid, the maximum sensitiveness of the ordinary alcohol reaction being 1:1,000. A blank test should always be made as a precaution. Comparable tests with a number of commercial tans (*e.g.* mangrove, pine-bark, oak-wood, mimosa and quebracho extracts) gave negative reactions, and it is concluded that there is present in the tannin idioblasts another substance which is associated with the tannin, and which is responsible for the precipitation. J. G.

Comparative Study of Juices from Frozen Fruits. T. A. Pickett. (*Ind. Eng. Chem.*, 1932, **24**, 353–354.)—Blackberries, cherries, dewberries, peaches, pears, plums, raspberries, and strawberries were examined fresh, and after slow and quick freezing for varying periods. The juices were expressed, centrifuged, and tested for hydrogen-ion concentration and titratable acidity, and in many cases for the freezing-point depression, conductivity and total solids. The juices from all these fruits, frozen and tested immediately, had greater titratable acidities than the juices from the fresh fruits; apparently this is due to a breaking down or increased permeability of the cells upon freezing. Further, the titratable acidity increases as length of time of storage increases, partly owing to dehydration. Since the juices of fruits frozen and stored at −12·2° C. have greater titratable acidities than those frozen at −73·3° C., and stored at −12·2° C., the juices of the fruits frozen at the lower temperature more nearly resemble the fresh juices in this respect. The freezing-point depression figures follow the same lines as those for the acidities. D. G. H.

Quantitative Determination of Laevulose and Sucrose. J. Fiehe. (*Z. Unters. Lebensm.*, 1932, **63**, 288–291.)—Solutions of various concentrations of a number of sugars were heated for 30 minutes on the water-bath with 10 c.c. of 5 *N* hydrochloric acid (in such a manner as to avoid over-heating), the cooled liquid was diluted to 50 c.c., and 5 c.c. were mixed with 5 c.c. of 32 per cent. hydrochloric acid, and shaken with 30 c.c. of a 0·625 per cent. solution of phloroglucinol in 16 per cent. hydrochloric acid. The resulting hydroxy-methyl-furfural-phloroglucinol compound ($C_{12}H_{10}O_5$) was filtered off after 24 hours, washed with 20 c.c. of water, and weighed after 3 hours at 110° C., and 3 hours in air (*cf.* Fiehe and Kordatzki, ANALYST, 1929, **54**, 241; 1932, **57**, 254). Solutions (1 per cent.)

of dextrose, maltose, lactose, and wheat starch gave a yellow colour, and arabinose a blue-green colour, but no precipitate. Ten c.c. of a 1 per cent. solution and 5 c.c. of 2·3 and 4 per cent. solutions of sucrose yielded 12·36, 12·26, 20·40, and 27·65 mgrms. (means) of precipitate, respectively; 10 c.c. of 0·5 per cent. and 5 c.c. of 1, 1·5 and 2 per cent. solutions of laevulose yielded 11·07, 11·71, 18·70, and 26·65 mgrms., respectively. Results reproducible to within about 0·5 per cent. are obtainable if not less than 11 mgrms. of precipitate are weighed. The results indicate that 50 mgrms. of sucrose correspond with 26·3 mgrms. of laevulose if 10 c.c. of a 1 per cent. solution of the former are taken. The weight of precipitate obtained is not directly proportional to the amount of sugar taken, relatively higher results being obtained for the more concentrated solutions. J. G.

Modification of the Seliwanoff and Ihl-Pechmann Reactions for Laevulose. C. I. Kruisheer. (*Rec. Trav. Chim. Pays-Bas*, 1932, **51**, 273–278.)—These colour reactions are not specific for laevulose, since similar colorations, although of less intensity, are given by dextrose, galactose, lactose, and some other sugars. The disturbing influence of monosaccharides may be removed by oxidising these to the hexonic acids by the action of hypoiodite, eliminating the excess of iodine by adding sodium sulphite, and precipitating the iodides as cuprous iodide. Removal of the influence of disaccharides presents greater difficulty, which has not been entirely overcome. The hypoiodite treatment annuls the free aldehyde group of lactose, maltose, etc., and diminishes the disturbing effect by one-half. Preliminary heating with hydrochloric acid is unsatisfactory, as it not only destroys part of the laevulose, but yields a certain amount of hydroxy-methyl-furfural, which resists the oxidising action of the hypoiodite. The procedure outlined above diminishes not only the disturbance due to carbohydrate other than laevulose, but also that due to other extraneous substances, this being of especial advantage in urine analysis.

With pure sugar solutions, 2 c.c. of the liquid (containing not more than 2 per cent. of sugar) are treated in a 50-c.c. Erlenmeyer flask with 0·5 c.c. of 4 *N* sodium hydroxide solution and 2 c.c. of 0·1 *N* iodine solution [13 grms. of iodine and 15 grms. of potassium iodide to 100 (? 1000) c.c.], and, after 5 minutes, with 4 c.c. of 12 *N* hydrochloric acid and 4 c.c. of copper sulphate solution (25 grms. of $CuSO_4$, $5H_2O$ to 100 c.c.). Sodium sulphite solution (20 grms. of Na_2SO_3, $7H_2O$ to 100 c.c.) is then added until the liquid assumes the cream colour of cuprous iodide, large excess being avoided. The liquid is transferred to a test-tube, and, when the precipitate has settled, 8 to 10 c.c. of the clear or almost clear solution are pipetted off and treated, in a roomy test-tube, with either 10 drops of a 20 per cent. solution of resorcinol in alcohol (Seliwanoff test, *Ber.*, 1887, **20**, 181), or with 10 drops of a 20 per cent. solution of diphenylamine in alcohol (Ihl-Pechmann test, *Chem. News*, 1881, **51**, 114). The vessel is immersed in a boiling water-bath for 15 minutes; the appearance of a red (resorcinol) or blue (diphenylamine) colour indicates the presence of free or combined laevulose. With small amounts of the sugar the colour is rendered more distinct by shaking the cooled liquid with 2 c.c. of pure amyl alcohol or liquid phenol. The diphenylamine test responds to 0·002 per cent. of laevulose, but the resorcinol test is somewhat less sensitive;

both give negative results with 2 per cent. of dextrose, mannose, galactose, xylose, or arabinose.

In the case of urine, 80 c.c. are treated with 30 c.c. of half-basic lead acetate solution, and either centrifuged or left to settle; 25 c.c. of the clear liquid are mixed with 11·5 c.c. of saturated sodium phosphate solution, and again allowed to settle, 1 c.c. of the clear liquid thus obtained being oxidised with hypoiodite, and treated further as described above. Under these conditions, normal urine (with or without 4 per cent. of added dextrose) and diabetic urine (with 1·05 per cent. of dextrose) give no colour reactions, but urine containing 0·05 per cent. of laevulose reacts distinctly, and one with 1 per cent. of lactose just perceptibly. T. H. P.

Origin of Honey Diastase. J. Fiehe. (*Z. Unters. Lebensm.*, 1932, **63**, 329–331.)—The author considers that the diastase in honey is derived principally from the plant juices (*e.g.* the nectar), and, to a less extent, from the bees. This is contrary to the conclusions of certain other workers, but it may explain the low diastatic values obtained as a result of feeding with sugar, and the relatively high values from heather or buckwheat honeys. Hence honey which contains only bee diastase and relatively little plant diastase may sometimes behave like heated honey in the diastase test. Two similar samples of rosemary (*Rosmarinus officinalis*) honey from Narbonne contained 18·95 and 18·35 per cent. of water, and 2·29 and 1·26 per cent. of sucrose; the polarisation readings were — 3·0° and — 1·5° before, and — 3·4° and — 1·72° after inversion. Fiehe's test was negative, and the diastase values were 1·0 and 0, respectively. J. G.

Accidental Presence of Acrolein in Cider "Brandies." G. Warcollier and A. Le Moal. (*Compt. rend.*, 1932, **194**, 1394–1396.)—Brandies obtained by distilling cider or perry are normally free from acrolein, but in those of last season from 0·12 to 1·66 grm. per litre (18·1 to 255·4 grms. per hectolitre of absolute alcohol) was found for cider spirit, and 0·625 grm. per litre (86·0) for perry spirit. The acrolein may be formed from the glycerol by the action of *B. amaracrylus*, which occurs in water and causes bitterness in wines, or of organisms of the *B. Welchii* group. Acrolein is detected by means of: (1) Codeine, which gives a transient green coloration. (2) Voisenet's reaction with acid-albumin, hydrochloric and nitrous acids, which give a green coloration with from 0·1 to 1 mgrm. of acrolein per litre. This reaction fails if the proportion of acrolein is high, or if much acetaldehyde is present. (3) Arnold and Mentzel's reaction with phenylhydrazine hydrochloride and ferric chloride, which give a red colour with acetaldehyde or a green colour with acrolein (not less than 1 mgrm.). Normally, cider and perry spirits contain only traces of acetaldehyde, and the red colour rapidly gives way to the green if acrolein is present. (4) If the ferric chloride of reaction (3) is omitted, a green colour of intensity proportional to the acrolein content appears after 12 to 24 hours. (5) The Schiff–Gayon reaction. This may be made specific for acrolein if applied to a solution rich in sulphuric acid. To 5 c.c. of solution containing at least 2 mgrms. of acrolein are added 5 c.c. of sulphuric acid (dilution 1+1), the tube being shaken under cold water. Addition of 4 c.c. of Schiff–Gayon reagent then yields a persistent, apple-green coloration, which gives quantitative results when compared with solutions containing 1 to 10 grms. of acrolein per 1000 of 95 per cent. (by vol.) alcohol. T. H. P.

Fatty Acids and Component Glycerides of some Oleo Oils. A. Banks and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1932, **51**, 111–116T.)—Three North American oleo oils from three centres of production were analysed, and an examination of the glyceride structure showed that the fully-saturated components of the oleo oils are richer in palmitic and myristic acids than those of the original tallows. Whilst the oleo oils, as a whole, contain more palmitic (with myristic) acid, the total amount of stearic, oleic and linolic acids (68–70 mols. per cent.) is much the same as in many tallows. The proportions of palmitic (with myristic) acid (30 mols. per cent.), and of the total C_{18} acids (about 70 mols. per cent.) in the not fully saturated components of the oleo oils are very similar to those for the same class of glycerides in the tallows themselves, suggesting the approach to constancy of the not fully saturated glycerides of cattle-storage fats. These results are to be expected as a result of pressing the whole fats, which will leave behind the glycerides of higher melting point, in which stearic acid will predominate, although a lower melting-point component will exert solvent power on a closely-related derivative of higher melting-point, so that, in practice, no quantitative separation will occur. D. G. H.

Solubility of Vanillin and Coumarin. R. M. Hitchens. (*Ind. Eng. Chem.*, 1932, **24**, 418–419.)—The solubility of vanillin in cold dilute ethyl alcohol is low, but it rises rapidly with increase in the alcohol concentration and the temperature. With 70 per cent. alcohol the solubility is 76·7 grms. per 100 c.c. of solution at 40° C. Vanillin melts under ethyl alcohol at 50° C. Coumarin is much less soluble in ethyl alcohol solutions. Vanillin is not very soluble in glycerol solutions, and the solubility does not rise suddenly with increase of glycerol concentration and temperature. The highest value obtained was 11·4 grms. per 100 c.c. of solution; the maximum solubility of coumarin in glycerol solution was found to be 1·68 grms. per 100 c.c. W. P. S.

Existence and Distribution of Caffeine and Theobromine in Guarana. G. Bertrand and P. de Berredo Carneiro. (*Bull. Soc. Chim.*, 1932, **51-52**, 284–288.)—An examination of the seeds, leaves, roots, stems and buds of guarana (*Paullinia cupana*) has been made, particularly with reference to the proportions of caffeine and theobromine. The seeds consisted of 83·5 per cent. of kernel, containing: water, 11·02; fatty extract, 2·68; ash, 2·07; and caffeine, 3·91 per cent. No theobromine was found either in the kernels or in paste made from kernels. The following results are calculated on the dry material:

		Theobromine Per Cent.	Caffeine Per Cent.
Seeds		—	3·91
Leaves		1·20	0·38
Roots	Central cylinder	—	0·27
	Bark	—	1·74
Stems	Wood	—	0·19
	Bark	0·98	0·17
Buds	Flowers	1·54	—
	Flower stalks	0·38	

Both theobromine and caffeine are regarded as being formed in the leaves and in the green cells of the stem bark. In the flowers the degree of methylation of the xanthine does not proceed further than the formation of theobromine, and, once formed, both theobromine and caffeine may be translocated, but the slighter solubility of the theobromine may partly account for its less general distribution. The presence of both substances in the leaves is significant, seeing that caffeine only is present in tea, maté, coffee, *Ilex cassine*, and the leaves of *Neea theifera*.

D. G. H.

Detection of Diacetyl and Methyl-Acetyl Carbinol in Foodstuffs, etc. H. Schmalfuss and H. Barthmeyer. (*Z. Unters. Lebensm.*, 1932, **63**, 283–288.)—The authors' method (*Z. physiol. Chem.*, 1928, **176**, 282; *Biochem. Z.*, 1929, **216**, 330) is applied as follows:—*Diacetyl.*—Tobacco (3 grms.) is burned in a clay pipe, and the vapours are drawn through two wash-bottles containing 3 c.c. of 10 per cent. sulphuric acid. The resulting liquid is then mixed with 0·33 c.c. of 20 per cent. hydroxylamine hydrochloride and 0·2 c.c. of 1·27 per cent. nickel sulphate ($+7H_2O$) solutions, and 25 per cent. ammonia is added until the liquid is slightly alkaline. It is then heated for 1 minute and cooled, and the red nickel dioximine (Tschugaeff, *Z. anorg. Chem.*, 1905, **46**, 144) is removed by filtration and washed with a little alcohol and weighed; 0·26 grm. (of nickel dioximine) was obtained from 1 kilo. of tobacco. Coffee is ground and shaken with 500 c.c. of saturated salt solution in a 1500-c.c. flask, and the contents are heated, at a temperature which is increased gradually from 110° to 150° C., in a current of carbon dioxide. Two 50-c.c. portions are collected and saturated with salt, and the process is repeated, the final distillate (8 c.c.) being treated as described; 60 grms. of Costa Rica coffee yielded 1·1 mgrm. One kilo. of Dutch cocoa and 4 litres of dark beer each yielded 1·2 mgrm.; 5 litres of milk, soured with *S. acidi lactici* and *S. cremoris*, 2·1 mgrms.; 1 kilo. of butter, 0·1 to 0·6 mgrm.; and 5 kilos. of heather honey, 0·1 mgrm. of precipitate (m.pt. 232·5 to 236° C., according to the source).

Methyl-acetyl Carbinol.—Fifty c.c. of the residue after distillation are treated with 50 c.c. of 50 per cent. ferric chloride solution in order to convert the methyl-acetyl carbinol into diacetyl, which is determined as before. In all cases allowance is made for any blank. Deposits from the fermentation of cane and grape sugar with bakers' yeast, China tea, and black bread, gave negative results. J. G.

Rapid Method for the Determination of Nicotine in Unfermented Tobacco. O. Dafert and M. T. Bollbecher. (*Z. Unters. Lebensm.*, 1932, **63**, 331–333.)—The tobacco is dried and powdered, and 2 grms. are shaken well for 2 hours in a dry 50-c.c. stoppered flask with 2 c.c. of sodium carbonate solution (strength not stated), 40 grms. of trichloroethylene, and a little talc. The mixture is then filtered through a dry paper and ammonia is removed from 30 grms. of the filtrate (=1·5 grm. of tobacco) by a passage of a current of air for 2 minutes, the solvent being then removed from the residual liquid by slow evaporation in the presence of 10 c.c. of 0·1 *N* sulphuric acid. When the odour is no longer apparent, water is added to the residue to make a volume of 10 c.c., the liquid is filtered (to remove chlorophyll and resinous substances), and the nicotine is determined by means of an immersion-refractometer calibrated against a solution

containing 0·1 per cent. of pure nicotine sulphate and pure 0·1 *N* sulphuric acid. The maximum errors for 0·76 to 5 per cent. of nicotine (on the air-dried sample) are ±0·05 per cent. (compared with Shedd's method). The method of Bodnár, Straub and Nagy (*Biochem. Z.*, 1928, **195**, 103; 1929, **206**, 410) gives high results, and that of Brezina (*Chem. Zentr.*, 1917, I, 700) is also unreliable. J. G.

Removal of Nicotine from Tobacco Smoke. J. Traube. (*Chem. Ztg.*, 1932, **29**, 287.)—Absorption of nicotine and other poisons from tobacco smoke is effected by introducing a sufficiently thick layer of silica gel into the mouthpiece of the pipe or the holder of cigar or cigarette. Nicotine has a strong effect in lowering surface tension. With a stalagmometer the drop number was found to be 42·0 for water, and 47·6 for a 0·16 per cent. solution of nicotine. The efficiency of silica gel in removing nicotine from smoke has been demonstrated by passing the smoke through water, with and without the use of silica gel, and then testing the drop number. Without silica gel the drop number rose to 56, but, with it, was only 45 after the smoke from ten cigarettes had been passed through it.

R. F. I.

Determination of Nitroglycerin in Drug Preparations (Acid Distillation Method). E. L. Anderson. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 140–145.)—Colorimetric methods for this determination are unsatisfactory, and the ether extraction method, which has been in use during the past two years, has not given good results. The alcohol aliquot method will give high results if other alcohol-soluble nitrogenous constituents are present. The method now described is based on the volatility of nitroglycerin with steam, as it is distilled directly from a slightly acid solution of the sample into an alkaline solution, in which it is saponified. It is then reduced with Devarda's alloy, and the resulting ammonia is distilled into standard acid solution. Difficulty was experienced with this second distillation. When a Murray scrubber (*J. Amer. Pharm. Assoc.*, 1924, **13**, 423) was used as a trap in the neck of the distillation flask, blank experiments gave distillates requiring from 0·5 to 1·5 c.c. of 0·02 *N* sulphuric acid for neutralisation. These volumes were reduced to 0·1 to 0·5 c.c. by inserting, as a second trap, a 300-c.c. Kjeldahl flask containing 25 to 30 c.c. of water, and surmounted by a third trap of the type used in Kjeldahl distillations; the water in this Kjeldahl flask trap was kept heated during the distillation of the ammonia.

Sufficient of the tablets or solution to represent 0·05 grm. of nitroglycerin is mixed in an 800-c.c. Kjeldahl flask with 50 c.c. of saturated sodium sulphate solution (to raise the boiling point and prevent charring), 150 c.c. of water, and enough 10 per cent. sulphuric acid (5 to 10 drops) to give an acid reaction to litmus. This is distilled, through a trap and condenser, into an 800-c.c. Kjeldahl flask containing 30 c.c. of 5 per cent. sodium hydroxide solution, into which the outlet tube dips; a medium flame is used until the air is expelled, and then a large flame, the distillation occupying about 1 hour. The condenser is then washed with about 100 c.c. of water into the collecting flask. After addition of 2 grms. of Devarda alloy, the ammonia is distilled into 25 c.c. of 0·02 *N* sulphuric acid; 1 c.c. of this acid≡0·001514 grm. of nitroglycerin. This procedure gives good results, provided that great care is given to the details of the operations. T. H. P.

Behaviour and Identification of Arecoline and its Use as a Taenicide, with some Comparisons with Pelletierine. C. D. Howard. (*Amer. J. Pharm.*, 1932, **104**, 170–175.)—Arecoline is the active alkaloid of the areca nut, and the dosage for tapeworm in dogs is variously given as 1 to 16 mgrms., whilst the dose for pelletierine tannate (from pomegranate root-bark) is about 0·3 to 0·4 grm. One $\frac{1}{8}$ grain tablet of arecoline, administered to a guinea-pig of 350 grm. in weight, caused, in 5 minutes, paralysis of the rear limbs, but after half-an-hour recovery began. The administration of $1\frac{1}{4}$ tablets (10 mgrms.), however, on 3 occasions, caused death in 5 hours, after preliminary apparent recovery. Arecoline and pelletierine preparations resemble one another in many respects, but they may be distinguished by the smaller dose of the former, and the fact that it is usually met with as the hydrobromide, whilst pelletierine is used as the tannate; also by the odour of pelletierine base on distillation, the readier and more distinctive crystallisation of arecoline salts from alcohol and chloroform, the failure of picric acid to precipitate arecoline in dilute solution, and the more pronounced myotic action of arecoline. Moreover, sulphuric and selenious acids give a deep rose-red colour with pelletierine, deepening on heating, and eventually changing to a dirty olive-green, whilst with arecoline a bright yellow colour results. The melting-point of arecoline hydrobromide (anhydrous needle-shaped prisms or plates) is 167°–168° C., and that of pelletierine picrate is 150° C. Further reactions of arecoline and pelletierine include the following:—With potassium bismuthous iodide a crimson precipitate in faintly acid solution, and a distinct turbidity in 1 in 20,000 solutions. Iodine in potassium iodide (Wagner's reagent) is next in sensitiveness, the limit being 1 in 5,000 for arecoline, and 1 in 10,000 for pelletierine. Mayer's reagent is not so sensitive, and phosphomolybdic acid gives a greenish-white precipitate with a 1 in 1000 arecoline solution. No precipitates are obtained with mercuric chloride, platinic chloride, auric chloride, tannic acid, lead acetate or lead subacetate in moderately dilute solution. D. G. H.

Reaction for Distinguishing Primary Cyclic Amines and its Application to Medicines. J. A. Sanchez. (*Ann. Chim. anal.*, 1932, **14**, 152.)—Primary cyclic amines may be distinguished from primary, secondary or tertiary fatty amines by the colour reaction with a furfural acetic reagent, prepared by adding glacial acetic acid to a saturated solution of furfural in cold water, in the proportion of 5 drops of acid to 100 c.c. of furfural. For a free amine 1 or 2 drops of furfural reagent are added to 1 drop of the liquid amine or to a few mgrms. of the solid, when a bright eosin-red or violet-red colour develops on mixing, and, if no colour is apparent, 1 drop of concentrated hydrochloric acid is added, since it intensifies the colour. With amines in combination, dissociation must first be brought about by hydrolysis, so that to 0·05 grm. of the amine are added 2 drops of 30 per cent. sodium hydroxide solution, and the mixture is heated until evaporated to dryness or until dense aromatic fumes appear, and, after cooling, 1 drop of furfural reagent and 1 drop of concentrated hydrochloric are added. The red or violet-red colour at once forms, giving an alcoholic solution of the same colour. The amine function may thus be demonstrated in such substances as antifebrin,

phenacetin, stibenyl, lactophenin, etc. Novocaine and tutocaine may be distinguished from stovaine, or cocaine from alipine. Similarly, atoxyl and arsenobenzenes may be identified. D. G. H.

Determination of Aluminium in Organic Materials. G. J. Cox, E. W. Schwartze, R. H. Mann, and R. B. Unangst. (*Ind. Eng. Chem.*, 1932, **24**, 403–405.)—A suitable quantity of the organic material is dried and incinerated at the lowest possible temperature, the ash is treated with water and hydrochloric acid, evaporated to dryness and, after the addition of hydrochloric acid and water, the silica is separated by centrifugal action. The liquid is decanted, 1 c.c. of nitric acid and 1 c.c. of 0·1 *M* ferric sulphate solution are added, and the mixture is evaporated to about 10 c.c., diluted with water to 60 c.c., and treated with 5 c.c. of 1 *M* mono-sodium phosphate solution and 2 c.c. of 0·04 per cent. bromophenol blue solution. Ammonia (7 *M*) is added until a permanent precipitate is formed, the *p*H is adjusted to 4·2 by the addition of 3 *M* sodium acetate solution, and the mixture is centrifuged. The liquid portion is discarded, and the precipitate is dissolved in 0·5 c.c. of 6 *M* hydrochloric acid, 1·25 c.c. of glacial acetic acid and 15 c.c. of hot water. Five c.c. of 6 *M* sodium hydroxide are added, the mixture is centrifuged, and the liquid is decanted through a double filter. [If two filter papers are used, the filtrate will not give a reaction for iron when tested with mercaptoacetic acid (thioglycollic acid) and ammonia]. After the precipitate has been washed with hot water the filtrate and washings are diluted to 100 c.c. Twenty c.c. of this solution are treated with 25 c.c. of a solution containing 1 grm.-mol. of ammonium acetate, 1 grm.-mol. of ammonium chloride, 80 c.c. of 0·1 per cent. ammonium aurin tricarboxylate solution and 60 c.c. of 6 *M* hydrochloric acid per litre; the mixture is boiled under a reflux condenser for one minute, cooled, sufficient 1·6 *M* ammonium carbonate solution (4·8 to 5 c.c.) is added to give a final *p*H of 7·1, the mixture is shaken to expel carbon dioxide, and, after twenty minutes, the coloration is compared with that of a solution containing 5 c.c. of 0·04 per cent. thymol blue solution and 8 c.c. of 6 *M* hydrochloric acid per 500 c.c. The amount of aluminium present is determined by reference to a curve plotted from the colorimetric readings obtained when various quantities of aluminium are subjected to the entire scheme of analysis, beginning with the ash.

W. P. S.

Aluminium Content of Foodstuffs Cooked in Glass and in Aluminium. G. D. Beal, R. B. Unangst, H. B. Wigman and G. J. Cox. (*Ind. Eng. Chem.*, 1932, **24**, 405–407.)—Foods were cooked in glass (Pyrex) and in aluminium, and the average increases in the amounts of aluminium were determined (see preceding abstract). A negligible amount is taken up by neutral foods; acid and alkaline foods have more action. In no case is sufficient aluminium dissolved from utensils to interfere seriously with phosphorus absorption in an animal consuming the food. An average daily human intake of aluminium, when all foods are cooked in aluminium, is estimated at 12 mgrms., of which about 5 mgrms. are derived from the utensils. The increase in aluminium content varies from *nil* in potatoes boiled whole in their skins to 49 parts per million in apricots cooked for 40 minutes. The largest amount was 118 parts per million in "apple butter," which had been

cooked for 6½ hours in an aluminium vessel. A selection of other figures is as follows:—*Oatmeal*, cooked for 150 minutes in a glass vessel, a content of 1·48 parts per million of aluminium, and cooked in aluminium 8·8 p.p.m.; *creamed cabbage*, cooked for 45 minutes in glass, contained 0·37 p.p.m., and in aluminium 2·78 p.p.m., but, when cooked with sodium carbonate, there was an increase of 90·5 p.p.m. *Orange marmalade*, cooked for 90 minutes, in glass, gave 0·3 p.p.m., and in aluminium 3·06 p.p.m. *Cranberry sauce*, cooked for 10 minutes with sugar in glass, gave 0·6, and in aluminium 3·2 parts per million, but in aluminium without sugar 7·9 p.p.m. *Fried bacon*, cooked 5 minutes in glass, gave 0·25, and in aluminium 0·68 part per million. J. W. B.

Biochemical

Determination of Glutamine in the Presence of Asparagine. A. C. Chibnall and R. G. Westall. (*Biochem. J.*, 1932, **26**, 122–132.)—Attention is called to the fact, previously discovered by Schulze and Bosshard (*Landw. Versuchs-Stat.*, 1883, **29**, 305) and Thierfelder and von Crämm (*Z. Physiol. Chem.*, 1919, **105**, 58), that glutamine reacts abnormally with nitrous acid. It gives 92 per cent. of its total nitrogen as amino-nitrogen in the Van Slyke apparatus. The stability of glutamine in solution at 100° C. at various *p*H values has been investigated by determinations of both the amide-nitrogen and the amino-nitrogen. After being heated at 100° C. at *p*H 8 for 3 hours, glutamine gives 35 per cent. of the total nitrogen as amide-nitrogen, whilst the amino-nitrogen falls to 8·5 per cent. Asparagine is stable under these conditions. This difference in behaviour has been made the basis of a method for the separate determination of asparagine and glutamine in plant extracts. The method has been applied with success to a mixture of asparagine and glutamine, and also to six plant extracts, the amide contents of which were known from the previous work of Schulze. After investigation for possible sources of error, and bearing in mind the limit of accuracy with which the amino-nitrogen of a plant extract can be determined, it is recommended that the glutamine and asparagine content of a plant extract should be determined as follows:—(1) Glutamine amide-nitrogen + asparagine amide-nitrogen = increase in amide-nitrogen with *N* sulphuric acid. (2) Glutamine amide-nitrogen = increase in amide-nitrogen at *p*H 8 × 1·4. (3) Asparagine amide-nitrogen = (1)–(2). (4) The ratio "decrease in amino-nitrogen/increase in amide-nitrogen" at *p*H 8 should be about 2·3. (5) The ratio "glutamine amide-nitrogen/decrease in amino-nitrogen with *N* sulphuric acid" should be about 1. It will be raised if peptide-splitting occurs during the hydrolysis. (6) The presence of urea can be detected by an increase in the value of (2) if determined at *p*H 4. (7) The small error due to allantoin falls almost entirely on the value for asparagine amide-nitrogen. The instability of glutamine in aqueous solution offers an explanation of the low yields of crystalline glutamine obtained by Schulze from plant extracts. P. H. P.

Bromine Reaction of Pregnancy Urine. A. R. Armstrong and E. Walker. (*Biochem. J.*, 1932, **26**, 143–146.)—Voge (*Brit. Med. J.*, 1929, **2**, 829) suggested that Knoop's test for histidine, when applied to urine, offered a simple

test for pregnancy. Knoop's test consists in the addition of bromine water to the solution under examination to the point of maximum absorption, avoiding excess. On heating, a port wine-red colour develops, and fades slowly, on standing, and a black particulate precipitate is deposited. The reaction works best in faintly acid solution; the colour is modified, but not inhibited, by the presence of strong acids. The question arose whether the substance causing the reaction was histidine, as is always assumed. Therefore the authors have now isolated the substance in pregnancy urine which gives a positive reaction with bromine water (Knoop's test), and have identified it as histidine. No other substance has been found by them to give a Knoop reaction similar to that of histidine, and the only substance quoted in the literature is that of methylhistidine by Linneweh, Keil and Hoppe-Seyler (*Z. physiol. Chem.*, 1929, **183**, 11). The methylhistidine of Fargher and Pyman (*J. Chem. Soc.*, 1921, **119**, 734) does not give a positive Knoop test, but in this case the methyl group is attached to the amino-group, whereas in Linneweh, Keil and Hoppe-Seyler's methylhistidine the methyl group is attached to the ring. Therefore Knoop's test is considered to be specific for histidine and *N*-methylhistidine. P. H. P.

Milk Peroxidase. Its Preparation, Properties and Action with Hydrogen Peroxide on Metabolites. K. A. C. Elliott. (*Biochem. J.*, 1932, **26**, 10–24.)—It is generally believed that peroxidases are almost universally present in the tissues of animals and widely distributed in plants and bacteria, but it has not yet been shown experimentally that they serve any physiological function. It is even doubted whether their specific oxidising substrate, hydrogen peroxide, ever occurs significantly in normal living matter, but it is certain that hydrogen peroxide is formed by certain oxidising systems separated from living matter; it seems likely that hydrogen peroxide could be a normal tissue product. It was felt that more knowledge of the powers of peroxidase with hydrogen peroxide as an oxidising agent for substances of metabolic interest might throw light on its possibilities in a biological mechanism, and a study has been made to see what possible metabolites can be oxidised by hydrogen peroxide and an animal peroxidase under more or less physiological conditions. The separation of milk peroxidase by fractional precipitation with ammonium sulphate is described, whereby a crude, but considerably concentrated, preparation is obtained practically free from catalase. The activity of the preparation degenerates very slowly in the refrigerator at 0 to 5° C. (in 6½ months the activity of one sample dropped from a "purpurogallin number" of 3·6 to 2·4). The enzyme is active from about *p*H 4 to nearly *p*H 10. A colour appears to be associated with the enzyme, and haemochromogen bands can be obtained. Compounds which contain the –SH group, such as cysteine, glutathione and denatured proteins, interfere with tests for peroxidase with benzidine, guaiacum, and, to some extent, with *p*-phenylenediamine. This appears not to be an inhibition of the enzyme, as with hydrogen sulphide, but seems to be due to the reduction of the coloured reaction products by –SH compounds. A method for the determination of hydrogen peroxide in very small amounts (1 mgrm. in 35 c.c.), by the measurement of the evolution of oxygen by manganese dioxide, is described. The volume of gas obtained is affected by the

presence of proteins, phosphate, acid, etc., but in given conditions it is proportional to the hydrogen peroxide initially present. Conditions were devised by which nitrite could be oxidised quantitatively by hydrogen peroxide with peroxidase, as shown by the consumption of hydrogen peroxide and the disappearance of nitrite. Under similar conditions tyrosine and tryptophane were found to be oxidised to coloured products. Under the conditions in which nitrite is quantitatively oxidised no oxidation by hydrogen peroxide and peroxidase of the following substances was obtained: Formate, acetate, oleate, stearate, triolein, ethyl alcohol, glucose, glycerol, acetaldehyde, β-hydroxybutyrate, lactate, glycine, phenylalanine and histidine. Dihydroxyacetone and phenylglyoxal are oxidised by very dilute hydrogen peroxide without peroxidase. Thus the attempt to find any general activity of the system which might throw light on the physiological function of peroxidase has failed. Possibly the enzyme from milk may differ fundamentally from peroxidases found in active tissues, but this seems unlikely, since it is a very active enzyme, and will oxidise all the substances which are used in the ordinary qualitative tests for other animal peroxidases, and, in general, seems likely to have the same properties as they have. It is thought that it would be premature to suggest pigment-formation as a function of the enzyme. A study of the powers of a vegetable peroxidase as a catalyst of oxidations by hydrogen peroxide is now in progress. P. H. P.

Vitamin *A* and Carotene. IX. Conversion of Carotene into Vitamin *A* in the Cow. T. Moore. (*Biochem. J.*, 1932, **26**, 1–9.)—It has previously been shown that carotene, or some part of it, suffers conversion in the rat into the colourless vitamin *A*. The degree of yellow pigmentation of the body-fat of animals varies considerably between different species; thus the rat, sheep and pig possess colourless body-fats, whilst man, the ox and the fowl have more or less pigmented fats. It seemed desirable to examine the fate of carotene in animals of the latter group before reaching any conclusion as to the general applicability of results obtained with the rat. Both carotene and vitamin *A* have been shown to be present in the unsaponifiable fraction of New Zealand butter-fat, and, whereas the feeding of cows on carrots or green stuff leads to increases both in the carotene content and vitamin *A* activity of the butter-fat, the administration of cod-liver oil results only in increased vitamin *A* activity, and the degree of yellow pigmentation remains unchanged. These observations, which first seemed to support the view that no relation could exist between carotene and the vitamin, might now seem to point to an incomplete conversion of carotene in the cow, or even to an interchangeability of the functions of the pigment and vitamin in this animal. In the hope of shedding light on this question, two main lines of investigation have been followed:—(1) Specimens of liver, butter, etc., obtained from different cows, have been examined by the colorimetric method for carotene and vitamin *A*, and a comparison of specimens obtained from Jersey cows with those from other breeds has been made, since the Jersey cow is reputed to show unusually deep pigmentation in its body- and milk-fat. (2) The effects of giving carotene in the food, as carrots or red palm oil, have been studied on the degree of pigmentation and vitamin *A* content of butter-fat obtained from a cow at the end of the winter

stall-feeding period. The results show that, although the body-fat of the cow is normally characterised by the presence of small amounts of carotene, vitamin *A*, as such, is present in preponderating amounts, in both the liver-fat and the milk-fat. Since the cow is purely herbivorous, this finding suggests that carotene undergoes the conversion into vitamin *A* previously demonstrated in the rat. The conclusion is supported by the finding that the feeding of a cow with carotene, in the form of carrots, at the end of the winter stall-feeding period resulted in an increase, not only in the carotene content, but also in the vitamin *A* content of the butter-fat. The degree of pigmentation of butter-fat, when adequate carotene is available in the diet, is determined by breed. Butter-fat derived from Jersey cows gave a yellow value twice that obtained with butter-fat from Shorthorn cows under similar nutritive conditions. When the cow is at pasture the output of carotene and vitamin *A* in the butter-fat is very small in comparison with the amount of carotene available in the diet. Storage of vitamin *A* in the liver takes place, and a large excess of pigment must undoubtedly be excreted unchanged. It is noteworthy that, just as in the rat, the vitamin *A* content of the body-fat remains within normal limits in the face of large dietary excess of carotene, so in the cow the vitamin *A* and carotene of the butter-fat are maintained at normal values under similar conditions. On the other hand, during stall-feeding upon a diet almost devoid of carotene, the reserves of vitamin *A* available in the liver and elsewhere may be insufficient to meet the demands of prolonged lactation. In practical dairying a small allowance of carrots, or other material rich in carotene, should suffice to restore a positive balance. P. H. P.

Reduction Capacity of Plant Foodstuffs and its Relation to Vitamin *C*. III. Content of Reducing Substance in Different Fruits and Vegetables. J. Tillmans, P. Hirsch and J. Jackisch. (*Z. Unters. Lebensm.*, 1932, **63**, 241–267.)—The authors' method (ANALYST, 1932, **57**, 260) has been applied to about 130 samples of various fruits, vegetables, juices, preserves, and tinned foodstuffs, and the results are tabulated for extracts of the sample in a four-fold volume of cold water, or in 2 to 3 per cent. sulphuric acid, for 24 hours, and also at the b.pt. in the same solvents for 4 minutes. In some cases it was necessary to shake the liquid with a little nitrobenzene and to centrifuge the mixture, in order to remove most of the colour. In general, the hot sulphuric acid extracts gave the maximum titration values with the indicator, and these were closely parallel to the vitamin *C* values obtained from animal experiments recorded in the literature (Scheunert, *Der Vitamingehalt der Deutschen Nahrungsmittel*, 1929; Berg, *Die Vitamine*, 1927). Exceptions (*e.g.* with preserves or tinned foods) were traced to soluble metallic salts, but the high values from leaf vegetables do not appear to be due to the presence of any reducing substances other than those associated with vitamin *C*. Titration of the fresh extract with 0·001 *N* sodium thiosulphate solution 1 minute after the addition of an excess of 0·001 *N* iodine solution, in the presence of starch, gave values showing, as a rule, a close relationship with those obtained with the oxidation-reduction indicator. This method, however, is less specific, and the results are often high, particularly with old extracts. For the purposes of comparison the expression $10T/A$ was used,

where T is the maximum number of c.c. of 0·001 N indicator equivalent to 10 grms. of sample, and A is Hahn's guinea-pig unit (cf. *Z. Unters. Lebensm.*, 1931, **61**, 369, 545). The samples are classified as follows, according to the values of T:—Eight hundred to 100 c.c., parsley, green cabbage, Brussels sprouts, horseradish, kohlrabi and black currant; 100 to 50 c.c., chives, orange, lemon, elderberry, mountain ash, strawberry, red cabbage, mangold, cauliflower, green pea; 50 to 20 c.c., banana, blackberry, grapefruit, raspberry, red and white currants, mandarin, haw, gooseberry, spinach, white cabbage, leek, asparagus, tomato, turnip, radish, potato; 20 to 10 c.c., apple, bilberry, sweet and acid cherry, cranberry, quince, greengage, peach, plum, head lettuce, green bean, bayberry, melon, pumpkin, cucumber, beet; 10 to 1 c.c., apple, apricot, pear, dried fig, grapes, rhubarb, pickled cucumber, carrot, comfrey, celery, sugar beet, onion (*cf.* following abstract).

J. G.

Reduction Capacity of Plant Foodstuffs and its Relation to Vitamin C. IV. Reversibility of the Oxidation of the Reducing Substances in Lemon Juice. J. Tillmans, P. Hirsch and H. Dick. (*Z. Unters. Lebensm.*, 1932, **63**, 267–275.)—It is shown that the first stage of the oxidation of the reducing substances responsible for the vitamin C content of lemon juice (cf. *id.*, 1932, **63**, 1, 12, 21; Szent-Györgyi, *Biochem. J.*, 1928, **22**, 1387, and preceding abstract) is reversible. This oxidation may be carried out by means of 2·6-dichlorophenol-indophenol; by the passage of a stream of atmospheric oxygen for 3 hours at room-temperature, or for a shorter period at higher temperature; by the action of an equivalent amount of hydrogen peroxide for a few minutes in a boiling solution (its action for 1 hour at 0° and 25° C., respectively, produces only 5 and 50 per cent. of this effect); chlorine and iodine (*loc. cit.*) are also effective. Oxidation by air is irreversible, but the effects of the other reagents may be reversed if a stream of hydrogen sulphide is passed through the neutral or weakly acid solution for 5 minutes at 25° C., and the gas is allowed to remain in contact with the liquid in a stoppered flask for 24 hours, and the excess then removed in a current of nitrogen; the reversal is incomplete after oxidation with chlorine. Palladium-hydrogen is less effective, and in all cases the juices should be fresh, and prolonged contact with the oxidising agent should be avoided if it is required to restore the full reduction titration value (T). The results are supported by experiments on animals.

J. G.

Vitamin C Content of Orange Crush Beverage. E. M. Koch. (*Ind. Eng. Chem.*, 1932, **24**, 351–352.)—Orange crush is made by pressing fresh oranges and adding to the thick mixture of juice, pulp and some skin, sugar, lemon citric acid, small amounts of preservative, and a colour, storing the mixture at refrigerator temperature, and finally diluting a week's supply with tap or carbonated tap water. Oranges stored at refrigerator temperature were found to retain their vitamin C for at least 3 months; orange juice, unstrained, loses its antiscorbutic potency so rapidly that a test extending over 4 weeks shows a loss, and in 3 months destruction appears to be almost complete; a heavy crush syrup made from the juice unstrained, by adding sugar and preservative and acidifying with lemon citric acid, retains the vitamin as satisfactorily as the original fruit, but this syrup,

when diluted to 12 volumes with water, again rapidly loses its antiscorbutic properties. When the dilution of the crush was made in the laboratory with a minimum exposure to air and at room temperature, there was no detectable loss of antiscorbutic potency after storing for 10 days, so that a maximum interval of 10 to 14 days between dilution and consumption of the finished product assures the presence of antiscorbutic properties. It appears that the vitamin of the original juice is preserved by the high acidity and possibly by the high sugar content of the syrup. D. G. H.

Vitamin *D* Content of Red Palm Oil. W. J. Dann. (*Biochem. J.*, 1932, **26**, 151–154.)—A brief description is given of the fruits of the oil palms from which red palm oil is obtained. Four different samples of red palm oil, of which one was a native-rendered oil, whereas the others were "plantation oils" rendered by machinery in plantation factories, have been examined for their vitamin *D* content by the preventive method on albino rats. All four specimens were found to contain very little vitamin *D*. The richest of the four oils used (the native red palm oil) contained less than one-thirtieth as much vitamin *D* as an ordinary cod-liver oil. The red palm oils and cod-liver oils are, however, almost alike in their vitamin *A* activity. Therefore, the use is recommended of red palm oil as a convenient source of vitamin *A* free from vitamin *D* in nutritional experiments, and it appears likely that any sample of red palm oil, preferably of deep colour (*i.e.* particularly rich in carotene), having a low free fatty acid content (*i.e.* a plantation oil), could be used with safety. The native method of preparation of the oil involves its exposure in the open for long periods. If the palm fruit contains ergosterol, irradiation by the tropical sun might well transform a small amount of ergosterol into vitamin *D*, and thus native oils, in general, would be likely to contain more vitamin *D* than plantation oils. P. H. P.

Bacteriological

Growth of *Aspergillus versicolor* on Higher Paraffins. S. J. Hopkins and A. C. Chibnall. (*Biochem. J.*, 1932, **26**, 133–142.)—A mould has been found which will grow on synthetic higher paraffins as sole source of carbon. It is best described at the present time as a strain of *Aspergillus versicolor* (Buillemin) Tiraboschi. Its action on certain synthetic long-chain paraffins has been investigated, in the hope that information would be gained as to the manner in which the organism attacks a long carbon chain of this type, which has no polar group. The mould will grow on both odd- and even-number paraffins, but not on those with a longer chain than $C_{34}H_{70}$; it was only with great difficulty that growth could be obtained on *n*-tetratriacontane, $C_{34}H_{70}$. In experiments to find out the way in which the paraffin chain is attacked by the mould, a large scale culture on *n*-heptacosane, $C_{27}H_{56}$, did not yield any products of metabolism except carbon dioxide and mould mycelium. Indirect evidence has, however, been obtained from experiments with higher ketones on which the mould grew vigorously, and with secondary alcohols on which no growth was obtained at all. It appears that the primary product of oxidation of a paraffin is a ketone or

polyketone, and that further oxidation results in the production of shorter-chain fatty acids, which are then metabolised in the usual way. The scheme of metabolism excludes the initial formation of secondary or polyhydric alcohols, and in this respect only does it differ from the air oxidation of paraffins observed by Francis *et al.* (*J. Chem. Soc.*, 1922, **121**, 496; 2804). It is, of course, highly improbable that the paraffin chain could be oxidised at the terminal carbon atom, with the formation of a primary alcohol or *n*-fatty acid containing the same number of carbon atoms. P. H. P.

Effect of Carbon Dioxide on Bacterial Growth, with Special Reference to the Preservation of Fish. Part I. F. P. Coyne. (*J. Soc. Chem. Ind.*, 1932, **51**, 119–121T.)—Bacterial growth and autolysis chiefly account for the deterioration of fresh fish, and a study of the action of bacteria has been begun. Stock cultures were plated out on to horse heart agar, and single colony transfers were made into broth after incubation for 4 days at room temperature. Broth cultures were incubated for 3 days at room temperature, after which one loopful (platinum wire loop, 4 mm. diameter) was inoculated on to each plate, to be tested by making 7 successive strokes across the surface of the agar. Plates were tested in air, in hydrogen, in carbon dioxide, and in nitrogen. *Achromobacter*, *Flavobacter*, *Micrococcus*, *Bacillus* and *Pseudomonas* sp. all showed marked inhibition of growth in carbon dioxide, and the first three could not grow in strictly anaerobic conditions (hydrogen). Neither lack of oxygen nor *p*H value appears to account for the result, and further work is being carried out to establish the theoretical basis for the effect. The organisms inhibited by carbon dioxide are those which predominate in the normal bacterial flora of fish. D. G. H.

Agricultural

Evaluation of Sulphur Suspensions used in Spraying. R. M. Woodman. (*J. Soc. Chem. Ind.*, 1932, **51**, 103–107T.)—The methods of analysis of sulphur suspensions are examined, particular attention being given to the determination of total solids, total sulphur, and non-combined sulphur. The properties which a good sulphur suspension should possess are discussed. With many commercial suspensions the following determinations give useful results. *Total Solids.*—A portion of a well-shaken sample is weighed in a tared, well-stoppered weighing bottle, and evaporated to dryness at 100° C. *Total Sulphur.*—This is determined by the Hodsman's bomb method (*J. Soc. Chem. Ind.*, 1931, **50**, 391T) on 0·05 to 0·1 grm. of the dried residue powdered to pass a 100-mesh sieve. *Free Sulphur.* (*a*) *Carbon Disulphide Extraction Method.*—One to 2 grms. of the dried residue are extracted with several successive portions of 10 c.c. of carbon disulphide, the sulphur in the extract after evaporation of the solvent being finally dried at 100° C. This simple extraction method is not applicable to sulphur suspensions which contain protective colloid (*e.g.* "Sulsol" suspension), since the protective colloid prevents the sulphur from being quantitatively dissolved. The following modified extraction method was used for "Sulsol," acetone being used to coagulate the suspension: 10 c.c. of acetone were shaken with 10 c.c. of a diluted "Sulsol" suspension. After allowing 3 hours for sedimentation of coagulated solids, the

mixture was shaken with 20 c.c. of carbon disulphide, kept overnight, and the carbon disulphide layer was run off. Extraction with a further 20 c.c. of solvent was made, 3 or 4 days being allowed for the emulsion to "break" completely. The combined extracts were washed with water, the carbon disulphide was allowed to evaporate spontaneously, and the residue of sulphur was weighed after drying at 100° C. *Free Sulphur.* (*b*) *"Polysulphide" Method* (applicable to all sulphur suspensions).—Twenty-five c.c. of a diluted suspension (the total solids being less than 0·25 grm.) are mixed with 35 c.c. of sodium sulphite solution (10 per cent.), and heated on a water-bath for 45 minutes, with shaking every 10 minutes; 30 c.c. of strontium chloride solution (10 per cent.) are added, the liquid is filtered after 10 minutes, and the precipitate is well washed with boiling water until the filtrate amounts to nearly 300 c.c. An aliquot part of the filtrate, containing the sulphur as thiosulphate, is titrated with 0·05 *N* iodine solution. A correction for any thiosulphate originally present in the suspension is made by a method similar to the A.O.A.C. method (*A.O.A.C. Methods*, 1920, p. 68): 50 c.c. of the diluted suspension are mixed with 20 c.c. of ammoniacal zinc chloride solution, diluted to 300 c.c., thoroughly shaken, and kept overnight; the liquid is filtered, and an aliquot part titrated with 0·05 *N* iodine solution after neutralising with tartaric acid to methyl red indicator. The rate of sedimentation of three commercial sulphur suspensions was measured by determining the free sulphur in portions of the liquid withdrawn at different depths from a column of the suspension after a 22-hour period of sedimentation. S. G. C.

Determination of Minute Amounts of Boron in Soils. W. W. Scott and S. K. Webb. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 180–181.)—The following adaptation of published methods is described. *Separation of the Boron.*—One hundred grms. of soil (dried at 105° C.) are digested in 100 c.c. of boiling water, and the liquid is filtered. A small quantity of sodium carbonate is added to the filtrate, which is then evaporated to 25 c.c., transferred to a platinum dish, and evaporated to dryness, and the residue is ignited. The cooled residue is treated with 10 c.c. of phosphoric acid, and the contents of the dish are transferred, with the aid of 20 c.c. of methyl alcohol, to a 250-c.c. distilling flask fitted with a water-cooled condenser. The liquid is distilled from a water-bath, and the distillate is collected in a platinum dish. Ten c.c. of methyl alcohol are added to the flask, and the distillation is continued. Four to 6 drops of *N* sodium carbonate solution are added to the distillate, which is concentrated to 5 c.c., transferred to a small platinum crucible (25 to 30 c.c. capacity), and evaporated to dryness. *Colorimetric Determination.*—To the residue, 4 drops of concentrated hydrochloric acid and 0·5 c.c. of water are added, the solution is transferred to a small glass vial (30 mm. high), and diluted to 2 c.c. A strip of turmeric paper (45 × 3 mm.) is immersed in the liquid to a depth of 15 mm., and allowed to soak for 3 hours at 35° C. or, preferably, 24 hours at room temperature. The height (in mm.) of the red stain thus produced on the paper is compared with that of stains similarly produced by known amounts of boron in the form of boric acid. This method is suitable for determining 0·005 to 0·1 mgrm. of boron oxide; larger vials and longer strips of turmeric paper are required for amounts in the range 0·1 to 1·0 mgrm.

S. G. C.

Loss of Toxicity of Pyrethrum Dusts. F. Tattersfield. (*J. Agric. Sci.*, 1932, **22**, 396.)—The loss of toxicity of pyrethrum dusts on exposure to light and air is shown to be due to oxidation, and is greater with dusts than with powdered flower heads. The dusts were prepared by extracting the flowers with petroleum spirit and evaporating, the residue being taken up with absorbent earths. The toxicity was tested biologically, the bean aphis being used as a test subject. The loss of toxicity was tested, both biologically and by determining the ferricyanide reducing value, after exposure in thin layers under varying conditions. It was found that both light and air were necessary to cause loss; exposure to inert gases or *in vacuo* caused very little loss. Certain anti-oxidant compounds were found effective in protecting pyrethrum dusts against loss of toxicity on exposure. A dust to which 5 per cent. of hydroquinone had been added preserved its activity for 13 days, and even 1 per cent. had a definite effect. Colloidal sulphur and paraldehyde gave no protection. The following anti-oxidants were tested after being added to the dusts in the proportion of 2·5 per cent.:—Tannic acid, pyrocatechol, resorcinol and pyrogallol afforded a high degree of protection, whereas phenol and phloroglucinol gave little or none. Myrobalans and cutch powders gave some protection.

It appears that the superior stability of powdered pyrethrum flowers over dusts is due not to the presence of a stabiliser, but mainly to the larger size of the particles, or to the active principles being contained as cellular inclusions. R. F. I.

Water Analysis

Zinc in Water Supplies. E. Bartow and O. M. Weigle. (*Ind. Eng. Chem.*, 1932, **24**, 463–465.)—Some of the water supplies in the Missouri-Kansas-Oklahoma district contain up to 50 parts per million of zinc, but, although no ill effects have been observed in persons drinking these waters, it is suggested that a limit of 5 parts per million should remain the standard for drinking water.

W. P. S.

Organic Analysis

Use of Sinalbin as an Indicator. K. Harrison. (*Biochem. J.*, 1932, **26**, 88–89.)—Sinalbin, the glucoside of white mustard seed (*Sinapis alba*, Boiss.), may be used as an indicator. As shown by Will (*J. Pharm. Chim.*, 1872, 327), it develops an intense yellow colour with alkalis, which disappears on addition of excess of acid. For its preparation 400 grms. of the finely-ground seeds are extracted with carbon disulphide in a large Soxhlet apparatus until the extract is free from the yellow essential oil. The residue (200 grms.) is dried in air, and boiled for 30 minutes with 500 c.c. of 95 per cent. alcohol to inactivate enzymes; the alcoholic liquid is filtered hot, and, on cooling (preferably in ice-water), the glucoside crystallises out. A second extraction with hot alcohol gives a further yield. The crystals are filtered off, washed with a little ether, and twice re-crystallised from hot 98 per cent. alcohol; yield 4–5 grms. The stock indicator solution is of 0·5 per cent. strength; solutions in dilute (30 per cent.) alcohol keep

indefinitely, whereas aqueous solutions are liable to attack by moulds. The *p*H range is 6·2 (colourless) to 8·4 (yellow); the salt and protein errors are small. Sinalbin is suitable for the titration of weak acids and bases, and may be used with ammonia. It is affected by carbon dioxide in the cold, but may be used for the determination of carbonates in boiling solution; the carbonate must be run into a known excess of hot acid, and not *vice versa*. It should be useful for the micro-titration of some alkaloids, particularly quinine. P. H. P.

Vieböck and Schwappach Method for the Determination of Methoxyl and Ethoxyl Groups. E. P. Clark. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 136–140.)—Zeisel's method has certain limitations. The gravimetric determination of silver iodide involved occupies much time, and, if the material to be analysed or the reagents used contain sulphur, the silver nitrate solution must be replaced by pyridine, which is washed from the receivers when the reaction is completed. The solution is then evaporated to dryness, and the residue is dissolved in water and treated with silver nitrate. This procedure is, moreover, applicable only to methoxyl groups.

A volumetric method for determining methoxyl and ethoxyl groups, which is free from the above objectionable features, particularly the interference of sulphur, has been given by Vieböck and Schwappach (see Hans Meyer, *Analyse und Konstitutionsermittlung*, 5th Edit., 487), which the author now modifies in some details. The procedure follows Zeisel's method, except that the alkyl iodide is collected in an acetic acid solution of potassium acetate containing a little bromine. The following reactions then occur: $CH_3I + Br_2 \rightarrow CH_3Br + IBr$ and $IBr + 2Br_2 + 3H_2O \rightarrow HIO_3 + 5HBr$. The solution containing the iodic acid is washed into a flask containing a little sodium acetate, the excess of bromine is removed by means of formic acid, potassium iodide is added, the solution is acidified with sulphuric acid, and the iodine liberated is titrated with 0·1 *N* thiosulphate solution. As six atoms of iodine are liberated for each OCH_3 group, 1 c.c. of the thiosulphate is equivalent to about 0·5 mgrm. of methoxyl, so that 20 to 30 mgrms. of substance are ample for a macro determination. Micro determinations may be made in the same way with about 5 mgrms. of substance, 0·02 *N* thiosulphate being then used for titrating the iodine. Full details of the procedure and a dimensioned sketch of the apparatus used are given. Test analyses gave with α-methylglucoside (4·8 mgrms.) 15·9 (calculated 15·98) per cent. of OCH_3, and with monoacetyldihydrotoxicarol (5·44 mgrms.) 12·5 (calc. 12·5) per cent. T. H. P.

Determination of Methoxyl, Lignin and Cellulose in Plant Materials. M. Phillips. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 118–131.)—Brief summaries are given of the literature dealing with these determinations. For methoxyl, the modification of the Zeisel and Fanto apparatus (*Z. anal. Chem.*, 1903, **42**, 554) recommended is described, and the procedure followed is given in detail.

For lignin, the method used is that depending on dissolving the cellulose and other carbohydrates by means of fuming hydrochloric acid and weighing the residual lignin. An apparatus is described in which two separate 1-grm. samples of the material, previously extracted with a mixture of 32 parts of 95 per cent.

alcohol and 68 parts of benzene, and dried, are treated side by side with the acid. After the two residues of crude lignin have been dried and weighed, one of them is incinerated and the ash weighed; in the other the nitrogen-content is determined by the Kjeldahl method. Then, lignin = crude lignin − ash − (nitrogen × 6·25).

For determining the cellulose, use is made of the chlorine-treatment method. Two 1-grm. samples of the extracted and dried material are weighed in fritted glass crucibles, the weighings being made in weighing bottles. One of the crucibles is then fitted to a filter flask, and washed through with water, chlorine (water-scrubbed) being then passed through the crucible for 5 minutes, at the rate of one bubble per second. The material is next washed with dilute sulphurous acid, followed by water. The crucible is then placed in a 250-c.c. beaker filled with 2 per cent. sodium sulphite solution to within one-half inch of the top of the crucible, and the beaker is left on a steam-bath for 30 minutes. The second crucible is treated similarly, each being then washed with water under suction, and again chlorinated and digested with sodium sulphite solution. This procedure is repeated until the chlorinated material no longer gives the reddish-violet reaction of lignin chloride with sodium sulphite solution. Finally, the cellulose in the crucibles is bleached by adding 20 c.c. of 0·1 per cent. potassium permanganate solution, leaving at room temperature for 10 minutes, and rendering colourless with dilute sulphurous acid. It is then washed, successively, with very dilute ammonia solution, hot water, 95 per cent. alcohol, and ether, dried at 105° C., and weighed. On a weighed portion of the final product the ash is determined. The ash-free cellulose, thus determined, is reported as "Cross and Bevan cellulose." In some cases the pentosans in this cellulose are determined by the furfural method, cellulose less pentosans being returned as "pure cellulose." The assumption that all the furfural is derived from pentosans is not, however, justified. T. H. P.

Heat Test applied to Cotton and Linen Fabrics. M. Fort. (*J. Soc. Dyers and Colourists*, 1932, **48**, 94.)—This test is a rapid method for ascertaining whether the tendering of a material is due to acid treatment or to oxidation, where laundering, mercerising, or alkali boiling has removed not only the tendering agent, but also most of the degradation products. It consists in subjecting the fabric to dry heat in a small air-oven containing a white tile mounted on insulating supports on an upper shelf. The cuttings of fabrics are placed on the tile, and observations are made as to their rate of browning when compared with standard samples. The rate of heating the oven is from cold to 200° C. in 10 to 15 minutes. If acid is present on a fabric, browning may set in at 150° to 175° C. The test is also of value when only very small samples are available, *e.g.* those from damaged spots. R. F. I.

Inorganic Analysis

Determination of (Minute Amounts of) Copper. L. C. Hurd and J. S. Chambers. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 236–238.)—Clarke and Jones described (ANALYST, 1929, **54**, 333) a new colour reaction of copper, in which a "permanganate" colour (sensitive to 1 part of copper in 10,000,000 parts of water) is produced when ammonium persulphate and a trace of silver nitrate are added

to a very dilute feebly alkaline solution of a cupric salt containing dimethylglyoxime. The various factors contributing to the development of the colour and the use of the reaction for quantitative colorimetric purposes have been exhaustively studied. For satisfactory results it is necessary to adhere closely to the original directions. The colour produced is almost identical with that of a dilute permanganate solution. Since the original statement that the colour shows a tendency to fade on keeping was confirmed, the authors favour for the colorimetric comparison a series of secondary standards of potassium permanganate, with which the colour produced by the unknown quantity of copper can be rapidly compared. The relationship between the copper present and the number of c.c. of $N/500$ potassium permanganate solution present in the standard comparison solution required to match exactly the copper colour has been established, and is shown in graphical form. Sodium sulphate, magnesium sulphate, calcium sulphate, and potassium nitrate in a concentration of 2 mgrms. per c.c. do not appreciably affect the intensity or stability of the colour, but the chloride content should not exceed $0{\cdot}5\gamma$ per c.c. Iron and cobalt (in concentration of 2γ and $0{\cdot}02\gamma$ per c.c., respectively) interfere. S. G. C.

Determination of Lead in Rocks. G. v. Hevesy and R. Hobbie. (*Z. anal. Chem.*, 1932, **88**, 1–6.)—The finely-powdered rock (30 to 40 grms.) was treated with hydrofluoric and sulphuric acids in a gold basin until silica had been removed. To the residue was added a minute amount of radium *D* (an isotope of lead), the activity of which had been determined electroscopically. The radium *D* acts as an indicator for the completeness of the lead recovery, the activity of the lead after isolation being measured and a suitable correction applied, since the percentage recovery of the lead and that of radium *D* must be identical. The acid mass was diluted to 1500 c.c., the insoluble alkaline-earth sulphates collected and converted into carbonates by fusion with alkali carbonate, and the carbonates dissolved in acetic acid. The acetate solution and the original filtrate from the sulphates were treated separately with dilute silver sulphate solution, so as to contain 1 mgrm. Ag per 100 c.c., and precipitated hot with a slow current of hydrogen sulphide, which was maintained until the liquors were cold. The small sulphide precipitates were collected, united, and dissolved in nitric acid, the solution evaporated to dryness, the residue dissolved in $0{\cdot}001$ *N* nitric acid (20 c.c.), and the solution electrolysed for 20 minutes, a little urea being added. The anode (platinum wire 0·6 mm. in diameter) was heated before and after electrolysis at 250° C. and weighed on a micro-balance. For activity measurements the lead peroxide was dissolved in acetic acid, the solution evaporated to dryness on a watch-glass, and the residue tested in the electroscope. The activity of the added solution of radium *D* was measured under the same conditions. The average lead content of 222 different rock samples was found to be 0·0016 per cent.

W. R. S.

Internal Indicator for the Dichromate Titration of Iron. M. E. Weeks. (*Ind. Eng. Chem., Anal. Edit.*, 1932, **4**, 127–128.)—A 1 per cent. solution of *o*-bisanisidine in glacial acetic acid was applied as internal indicator in the usual procedure for the determination of ferrous iron by dichromate (stannous chloride reduction),

with satisfactory results. After reduction (one drop in excess of reducing agent), the solution was diluted with 400 c.c. of ice-cold distilled water, and treated with 12 c.c. of mixed concentrated phosphoric and sulphuric acids (1 : 1), 10 drops of indicator, and 30 c.c. of saturated mercuric chloride solution. The titration was carried out without delay, the end-point being reddish-brown. After a few minutes a blood-red colour develops. W. R. S.

New Colorimetric Method for the Detection and Determination of Chromium. G. C. Spencer. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 245–246.)—The test depends on the action of chromic acid in changing the crimson colour of wool dyed with Serichrome Blue R (Schultz, "Farbstofftabellen," 1914, dye No. 164) to a navy-blue shade, and is claimed to be suitable for detecting and determining in a semi-quantitative manner 0·01 to 0·1 mgrm. of chromium (as chromate) in 50 c.c. The dyed wool is prepared by shaking 2 grms. of woollen yarn or flock in a solution of 0·1 grm. of sodium sulphate, and 0·02 grm. of sulphuric acid in 40 c.c. of water, adding 20 c.c. of a solution of 100 mgrms. of the dye in 200 c.c. of water, and heating the mixture on a steam-bath for 30 minutes, after which the wool is filtered off, washed and dried. A number of colour standards are prepared by digesting on a steam-bath for 30 minutes 0·1 grm. of the dyed wool in 50 c.c. of water containing 3 c.c. of *N* sulphuric acid and a known amount of chromium added as a standard solution of potassium dichromate (1 mgrm. of chromium per c.c.), and subsequently filtering off, washing and drying the wool, and mounting it on a spot-plate with adhesive. In testing for chromium, this is separated, together with aluminium and iron, by precipitation as hydroxide. The precipitate is filtered off, washed, digested for 30 minutes in 30 c.c. of water containing 3 c.c. of *N* sodium hydroxide and 5 c.c. of hydrogen peroxide (U.S.P.), and the liquid is then heated until the peroxide is decomposed. The liquid is filtered, and to the filtrate (containing the chromium), 3 c.c. of *N* sulphuric acid and 0·1 grm. of the dyed wool are added. After digesting on a steam-bath for 30 minutes, the wool is filtered off, washed, and dried. The quantity of chromium present can be judged by comparison with the colour standards. Small quantities of tungstic, vanadic, and permanganic acids, ferrous sulphate, manganous sulphate, and chrome alum were found to cause no colour-change of the dye. S. G. C.

Detection of Beryllium in Rocks. G. Rienäcker. (*Z. anal. Chem.*, 1932, **88**, 29–38.)—The sensitiveness of Fischer's reaction with 1, 2, 5, 8-tetrahydroxyanthraquinone (ANALYST, 1928, **53**, 303) was confirmed. The following procedure was worked out for the detection and approximate determination of beryllia in rocks: 0·1 grm. of the finely powdered is fused with 1 grm. of sodium hydroxide for 5 to 10 minutes in an iron crucible. When cold, the crucible is cooled in ice, and the melt dissolved in water, ice being used to prevent the temperature from rising sufficiently to cause hydrolysis of the sodium beryllate. The liquid is filtered and the precipitate washed, the total bulk being 30 c.c. The filtrate, or an aliquot part, is adjusted with dilute sulphuric acid to about 0·33 *N* alkalinity, and treated with 12 drops of the reagent (0·01 per cent. solution in 96 per cent. alcohol). By repeating the test with decreasing aliquot parts of filtrate until the limit of sensitiveness of the reaction has been reached (3 to 5μ grm. in 15 c.c.), the original

beryllium concentration can be estimated. The method of decomposition employed ensures removal of the magnesia with the ferric hydroxide. The time required is about 45 minutes. W. R. S.

Separation of Beryllium from Aluminium by Guanidine Carbonate. A. Jílek and J. Kota. (*Z. anal. Chem.*, 1932, **87**, 422–437.)—Aluminium solutions are precipitated by guanidine carbonate; the precipitate is soluble in excess of reagent. The beryllium precipitate is insoluble in excess. In a solution containing ammonium tartrate, guanidine carbonate precipitates beryllium, but no aluminium. The weakly acid chloride solution, containing not more than 0·1 grm. of either oxide, is treated with 50 c.c. of ammonium tartrate solution (21·25 grms. of tartaric acid neutralised with ammonia and made up to 1 litre), and dilute potassium hydroxide solution till it is barely acid to methyl red. It is then stirred and treated at ordinary temperature with 150 c.c. of a filtered 4 per cent. solution of the reagent and 2·5 c.c. of 40 per cent., almost neutral, formaldehyde. The volume is made up to 250 c.c. The crystalline precipitate, which shows a silky lustre, is set aside for 12 to 14 hours, then collected, and washed with a solution containing 50 c.c. of the ammonium tartrate, 150 c.c. of the guanidine, and 2·5 c.c. of the formaldehyde, reagent. It is converted into and weighed as BeO, after ignition to constant weight. W. R. S.

Rapid Determination of Molybdenum in Steel. E. Bertrand. (*Bull. Soc. Chim. Belg.*, 1932, **41**, 98–103.)—Yellow *hydrated* tungstic acid is transferred by means of a pad of cotton wool to strips of filter paper (2 × 12 cm.), which are gently rubbed with the pad until covered with a uniform layer of the tungsten compound. Stannous chloride solution is made from 20 grms. of tin and 200 c.c. of strong hydrochloric acid; the solution is diluted to a litre. If a drop of dilute molybdenum solution is deposited on the prepared paper, and the spot treated with stannous chloride solution, a greyish-blue stain is obtained, the intensity and rate of production of this being proportional to the molybdenum concentration. The sensitiveness is stated to be 0·00005 mgrm. Mo in a drop of solution. The common acids and the metals met with in steel do not interfere; phosphoric acid bleaches the colour to some extent. Copper gives a stain, but this is much less intense; thus, 0·2 per cent. Mo can be detected in copper. The test is applied to steels in the following manner: one grm. is dissolved in 30 c.c. of warm hydrochloric acid (1:1), containing 25 c.c. of phosphoric acid per litre. The addition of phosphoric acid prevents the formation of insoluble tungstic acid. When dissolved, the iron is oxidised with 15 c.c. of 5 per cent. potassium chlorate solution. Chlorine is boiled off; the solution is diluted to 75 c.c., cooled, and made up to 100 c.c. A drop is placed on the test paper, which is then treated with stannous chloride. The stain is matched against others produced by steels of known molybdenum content. A colorimetric scale is prepared from ammonium molybdate solution (1·84 grms. per litre; 1 c.c. = 0·001 grm. Mo). Quantities of 0·25, 0·5, 1·0, 1·5, etc., c.c. are evaporated to dryness, and 1 grm. of steel free from molybdenum is added to each standard. The metal is dissolved, and the solutions are diluted to 100 c.c., as described above. The standard solutions, which are stable, are kept in reagent bottles provided with perforated rubber stoppers; each stopper holds a glass rod,

with which a drop of solution is taken. The drops of standard and assay solution are placed on the same strip of paper so as to be wetted at the same time when the tin solution is poured on. The steel used as a standard should, if possible, be similar in composition to that under examination. W. R. S.

Volumetric Determination of Molybdenum with Permanganate. E. Carrière and R. Lautié. (*Comptes rend.*, 1932, **194**, 1167–1168.)—Potassium molybdate (0·5 grm.) is dissolved in 150 c.c. of 18 per cent. sulphuric acid, and the solution reduced under carbon dioxide with 15 grms. of pure zinc wire at 50° to 60° C. The cooled liquid is filtered through zinc wool in an atmosphere of carbon dioxide into a conical flask and titrated with permanganate (3·15 grms. per litre). The results indicate reduction to Mo_2O_3. The degree of reduction remains unchanged if the amount of zinc and acid is increased. A higher acid : zinc ratio causes slightly stronger reduction, a deficiency in zinc incomplete reduction. Hydrochloric acid used instead of sulphuric gives less concordant results. W. R. S.

Determination of Vanadium in Alloy Steels. H. H. Willard and P. Young. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 187–190.)—*Chromium-Vanadium Steels.*—Four to 5 grms. of the steel are dissolved in hot dilute sulphuric acid (30 to 40 c.c. of water with 1·5 c.c. of concentrated sulphuric acid for each 1 grm. of steel, and 2 c.c. in excess), the solution is oxidised with nitric acid, boiled to expel nitrogen oxides, and cooled. Thirty c.c. of phosphoric acid (sp.gr. 1·37) are added, the liquid is diluted to 300 c.c., and an excess of 0·1 *N* permanganate solution (as shown by the pink colour of the solution persisting for 2 minutes) is added. Five c.c. of 0·1 *N* sodium azide solution are added, the liquid is boiled vigorously for 10 minutes, cooled, and 15 grms. of sodium acetate crystals are added (the addition of a few drops of sulphuric acid will be necessary if a permanent precipitate forms); 0·6 c.c. of diphenylbenzidine indicator solution (prepared by dissolving 0·1 grm. of diphenylbenzidine in 10 c.c. of concentrated sulphuric acid, and diluting with 90 c.c. of glacial acetic acid) is added, the solution is kept for 5 minutes to allow the blue colour to develop, and then titrated with 0·025 *N* ferrous sulphate solution until the indicator is discharged. A very sharp end-point is claimed. A correction to be applied for the indicator, amounting to 0·03 c.c. of the ferrous sulphate solution for each 0·1 c.c. of indicator, is *added* to the volume of ferrous sulphate used.

Steels containing Tungsten.—A modification of the above method is necessary when tungsten is present. Tungstic acid is kept in solution as a complex fluoride throughout the analysis. Twenty-five c.c. of water and 4 c.c. of concentrated sulphuric acid are added to a 1-grm. sample of the steel contained in a 400-c.c. beaker; the liquid is warmed gently until the steel is completely decomposed and the tungsten has separated as a black powder; 5 or 6 drops of concentrated nitric acid are then added, a swirling motion is imparted to the contents of the beaker, and 5 c.c. of hydrofluoric acid (48 per cent.), followed by 5 c.c. of nitric acid are added. A clear solution should thus be obtained; this is diluted to approximately 100 c.c., and boiled for 5 minutes, after adding 1 grm. of ammonium persulphate to complete the oxidation of the tungsten. Five c.c. of 0·1 *N* ferrous sulphate

solution are added, and the liquid is diluted to between 150 and 175 c.c. and cooled. The vanadium is now oxidised by the addition of an excess of 0·1 *N* permanganate solution. Five c.c. of 0·1 *M* sodium azide solution are added, and the liquid is boiled vigorously for 10 minutes and cooled; 3 c.c. of hydrofluoric acid (48 per cent.) and 0·3 c.c. of diphenylamine sulphonate indicator (prepared by dissolving 3·2 grms. of barium diphenylamine sulphonate in 1 litre of water, adding a slight excess of sodium sulphate, and decanting the clear liquid, which is used as the indicator solution) is added. The colour change of the indicator at the end-point is from purple to green. The correction to be applied for the indicator must be determined by carrying out analyses of a standard steel, the difference between the calculated volume of ferrous sulphate solution required for the known quantity of vanadium present and the volume actually used in the titration, representing the indicator correction to be *added* to the volume of 0·025 *N* ferrous sulphate solution used in the analysis of other steels. S. G. C.

Determination of Sulphur in Coal by the Perchloric Acid Method. G. L. Smith and A. G. Deem. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 227–229.)—The following new method for determining sulphur in coal is described:—To a 1-grm. sample of coal contained in a 300 c.c. Erlenmeyer flask are added 1 grm. of potassium nitrate, 5 c.c. of concentrated nitric acid, 0·16 grm. of ammonium vanadate (to act as a catalyst in the oxidation), 2 to 4 grms. of monochloracetic acid (to prevent subsequent frothing), and 15 c.c. of perchloric acid (70 per cent.). The whole is digested for 10 minutes at 120° C.; the temperature is raised to 180–185° C., and the heating is continued until the coal is oxidised, and an orange-red precipitate of vanadium pentoxide appears (this occurs usually within 10 minutes, but may take 25 minutes). After cooling, 5 to 10 c.c. of concentrated hydrochloric acid are added, and the liquid is heated until the orange-red precipitate is again obtained; 100 c.c. of water and 0·2 grm. of hydroxylamine hydrochloride are added, the liquid is heated to reduce the vanadium to the hypovanadate condition, filtered, and the sulphate in the filtrate, after dilution to 400 c.c., is precipitated by barium chloride in the usual manner. The results of numerous analyses recorded in the paper are low in tendency as compared with the results obtained by the Eschka method. S. G. C.

Determination of Germanium. J. H. Müller and A. Eisner. (*Ind. and Eng. Chem., Anal. Edit.*, 1932, **4**, 134–136.)—Germanic sulphide is quantitatively converted into the dioxide by hydrolysis with boiling water, hydrogen sulphide being evolved. Application of the reaction obviates the use of nitric acid for the oxidation of the sulphide, a practice involving risk of loss due to the violence of the oxidation. The sulphide precipitated from 6 *N* sulphuric acid solution under exclusion of air is left in contact with the hydrogen sulphide under a pressure of 2 ft. of water for 12 hours, the flask being connected with the generator. The precipitate is collected in a porous crucible, washed with *N* sulphuric acid, and freed from liquid by suction. The crucible is immersed in sufficient boiling water to cover it, and the liquid is boiled in the covered beaker until the precipitate has entirely dissolved. The crucible is removed and rinsed with water, the solution

is concentrated by evaporation, transferred to a tared porcelain crucible, and evaporated to dryness. The residue may be treated with nitric acid for oxidation of traces of free sulphur. It is ignited at 900° C. and weighed as GeO_2.

W. R. S.

Use of Potassium Manganate in Volumetric Analysis. H. Gall and M. Ditt. (*Z. anal. Chem.*, 1932, **87**, 333–338.)—Oxidimetric determinations with permanganate require an acid medium. It is shown that manganate can be applied to oxidimetric work in alkaline media. The manganate solution was prepared according to Gall and Lehmann's directions (*Ber.*, 1927, **60**, 2491; 1928, **61**, 670). The solution is standardised against sodium oxalate. For the determination of phosphorous or hypophosphorous acid the alkaline solution is treated with a distinct excess of manganate solution, and gently boiled for 10 minutes. A known amount of oxalic acid, approximately equivalent to the manganate, is then added, and the solution acidified with 25 per cent. sulphuric acid; the excess oxalic acid is then titrated at 60° C. with manganate. In acid solution the manganate liberates twice as much oxygen as in alkaline solution. W. R. S.

Volumetric Determination of Cobalt with Permanganate. J. Ledrut and L. Hauss. (*Bull. Soc. Chim. Belge*, 1932, **41**, 104–114.)—The precipitation of cobalt oxalate and the volumetric determination of the combined oxalic acid by means of permanganate have been studied. Serviceable results are claimed.

(ABSTRACTOR'S NOTE.—The precipitation of cobalt oxalate as a quantitative method has been adversely criticised, and is not used in standard analytical practice. *Cf.* Grossmann, *Die Bestimmungsmethoden des Nickels und Kobalts*, Stuttgart, 1913.) W. R. S.

Rapid Determination of Sulphur in Brass and Bronze. J. O. Cooney. (*Ind. and Eng. Chem., Anal. Edit.*, 1932, **4**, 33.)—The process is based on solution of the metal in cupric ammonium chloride and determination of the sulphur in the residue. The alloy (5 grms., as finely divided as possible) is digested with the reagent (1 part of the salt, 3 parts water, and acidification with 5 per cent. of hydrochloric acid) at gentle heat, with occasional stirring. When the action is over, the solution is filtered while hot through a sulphur-free asbestos mat under suction. Washing is done with 5 per cent. hydrochloric acid, then with water. The asbestos and residue are returned to the beaker with as little water as possible; an equal volume of strong nitric acid and 10 c.c. of bromine water are added. The action is brought to completion at boiling heat, the bromine is boiled off, and the asbestos is removed by filtration. The filtrate is evaporated to dryness with 0·5 grm. of sodium bicarbonate to dehydrate silica, the residue is dissolved in dilute hydrochloric acid, the solution is filtered, and the filtrate is treated with barium chloride. If lead or antimony is present, it should be precipitated with pure zinc and filtered off with the silica prior to the precipitation of the barium sulphate. W. R. S.

Detection of Nitrous "Oxides" in Sulphuric Acid. L. W. Marrison. (*J. Soc. Chem. Ind.*, 1931, **51**, 110T.)—Two c.c. of the sulphuric acid to be tested are poured into a mixture of 1 c.c. of aqueous sucrose (0·1 per cent.), and 0·5 c.c.

of alcoholic α-naphthol (5 per cent.). The sugar and the α-naphthol will yield a violet ring at the interface of the two liquids. If more than 5 parts per million of N_2O_3 are present in the acid, the lower layer will become green; if more than 0·06 per cent. of N_2O_3 is present, the upper layer will be coloured yellow. The test may be made approximately quantitative by using fresh standards of sodium nitrite in pure sulphuric acid. Nitrites in aqueous solution may be similarly detected by adding 2 c.c. of the solution to be tested to the sucrose-naphthol mixture and pouring in pure sulphuric acid. About 12 parts per million of N_2O_3 are detectable in aqueous solution. Ferrous iron interferes, about 300 parts per million of it giving a fair simulation of 6 parts per million of N_2O_3. Chromic and molybdic acids interfere. The following do not interfere: Chloride, bromide, sulphite, thiosulphate, acetate, borate, perchlorate, phosphate, sulphide, barium, calcium, strontium, copper, cadmium, zinc, mercury, lead, manganese, magnesium.

S. G. C.

Analysis of Nitrous Oxide by Solubility in Water. A. L. Chaney and C. F. Lombard. (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 185–187.)—The method is applied to the determination of nitrous oxide in the gas used for anaesthesia, and is a slightly modified form of that described by Bennett (*J. Phys. Chem.*, 1930, **34**, 1137); water saturated with air, nitrogen, or oxygen is used, instead of air-free water, for the absorption of the nitrous oxide, and a correction factor is introduced for the effect of this dissolved gas, instead of employing a graphical method of calculation of the percentage of nitrous oxide. S. G. C.

Microchemical

Carbohydrates. I. Micro-Determination of Carbohydrates in Pure Solutions, and in Animal Material. Z. Dische. (*Mikrochem.*, 1931, **10**, 129–189.)—A comparative description of the different micro methods of sugar determination in use, with complete practical details and references is given. The methods include: A. **Reduction Methods.** 1. *Reduction of Cupric Salts.*—The reduced copper oxide is filtered off, and may be determined titrimetically by dissolving in an oxidising acid reagent and titrating with potassium permanganate, as in the method of Fontes and Thivolle (*Bull. Soc. Chim. biol.*, 1927, **9**, 353). The reduced copper may also be determined iodimetrically by the Shaffer–Hartmann method (*J. Biol. Chem.*, 1920, **45**, 365; Somogyi, *ibid.*, 1926, **70**, 599; and Thompsett, *Biochem. J.*, 1930, **24**, 1148). Alternatively, the unreduced copper may be determined iodimetrically by the MacLean method, modified by Bang (*Biochem. Z.*, 1918, **87**, 248; 1918, **92**, 344), titrating finally with *N*/1000 thiosulphate solution. The reduced copper may also be determined colorimetrically by the Folin–Wu method (*J. Biol. Chem.*, 1919, **38**, 81; **41**, 367; Folin, *ibid.*, 1930, **82**, 83; *ibid.*, 1926, **67**, 357; Benedict, *ibid.*, 1926, **68**, 759; and 1928, **76**, 457).

2. *Reduction of Mercury Salts.*—The method has been worked out on the micro scale for biological material by Baudouin and Lewin (*Bull. Soc. Chim. biol.*, 1927, **9**, 280), and appears to be more rapid and more simple than the copper salt methods.

3. *Reduction of Ferricyanide.*—The reduction of ferricyanide is not so susceptible to back oxidation in the air as the copper salt methods, but is less specific. In the Hagedorn–Jensen method (*Biochem. Z.*, 1923, **135**, 46) the reduced ferricyanide is determined iodimetrically. Flatow (*Biochem. Z.*, 1928, **194**, 132) determines the excess ferricyanide by titrating with 0·2 per cent. indigo carmine solution, and Jonescu (*Bull. Soc. Chim. biol.*, 1928, **10**, 252) determines the reduced ferricyanide by titration with permanganate. The unreduced ferricyanide may be determined colorimetrically by Folin's method (*J. Biol. Chem.*, 1928, **77**, 421; 1929, **81**, 231; 1929, **83**, 115; ANALYST, 1928, **53**, 392; 1929, **54**, 246), or by the method of Van Slyke and Hawkins (*J. Biol. Chem.*, 1929, **84**, 69). The unreduced ferricyanide may also be determined gasometrically by the method of Van Slyke and Hawkins (*J. Biol. Chem.*, 1929, **79**, 739), in which the nitrogen developed by the action of alkaline hydrazine on potassium ferricyanide is measured.

4. *Methods Depending on the Reduction of Organic Substances.*—Chief of these methods is the reduction of acetone-picric acid, in the method of Benedict (*J. Biol. Chem.*, 1929, **48**, 50), and that of Sumner (*ibid.*, 1921, **47**, 5; 1925, **62**, 287; and 1925, **65**, 393). The colour developed is compared with a standard of similar sugar content. In Milroy's method (*Biochem. J.*, 1925, **19**, 746) nitro-anthraquinone sulphonic acid is reduced by the sugar to a red amino compound, in 10 per cent. potassium carbonate solution. Eisenhardt's method (*Münch. med. Wochenschr.*, 1920, p. 1382) depends on the reduction of methylene blue.

B. **Methods Depending on the Fermentation of Sugar.**—Sugar is fermented by yeast and micro-organisms, such as *B. coli*, to carbon dioxide. The method of Wagner (*J. Metabol. Res.*, 1925, **5**, 353) measures, in a Van Slyke apparatus, the carbon dioxide formed, and Grafe and Jorgenfrei (*Deutsch. Arch. klin. Med.*, 1924, **145**, 294), whose method is adapted for blood, use a Barcroft manometer.

C. **Osazone Methods.**—These methods are all colorimetric, and have been used on the micro scale by Dische and Popper (*Biochem. Z.*, 1926, **175**, 371), Dische [*Mikrochem.*, 1929, **1** (Neue Folg.), 1], Glassmann (*Z. physiol. Chem.*, 1925, **150**, 16), and Tillmans and Philippi (*Biochem. Z.*, 1929, **215**, 36).

D. **Methods Depending on Carbohydrate Reactions.**—Methods are based on the characteristic reactions of carbohydrates when heated with different organic substances, such as naphthol, indole, diphenylamine, thymol, phloroglucinol, in concentrated mineral acids. In these methods are also included special methods for determining different carbohydrates in admixture with each other.

II. DETERMINATION OF CARBOHYDRATES IN DIFFERENT ANIMAL MATERIALS.—The application of the methods to various kinds of biological material is discussed in detail, including different methods of removing the protein before the determination. J. W. B.

Micro-Determination of Phosphoric and Arsenic Acids with "Molybdenum-blue." S. Zinzadge. (*Z. für Pflanzenern., Düng. u. Bodenk.*, 1932, **23**, 447–454.)—The method is also described in other Continental journals, *e.g. Ann. agronomiques*, 1931, **43**, 321, *Bull. Soc. Chim.*, 1931, **49**, 872. It depends on

the use of a special "molybdenum-blue" reagent, and differs from the existing methods for phosphoric and arsenic acids involving the use of molybdenum compounds in that the reagent and the blue colour produced with these acids are both relatively stable. The reagent can be purchased in a proprietory form from Schering-Kahlbaum, A.G., of Berlin, or the Société des Usines Chimiques Rhône-Poulenc, of Paris, or may be prepared as follows: 120 c.c. of sulphuric acid (sp.gr. 1·785) are well mixed with 6·02 grms. of pure molybdic oxide powder in a porcelain dish; the mixture is heated and stirred until the molybdic oxide is dissolved; after cooling, 70 c.c. of water are added, the liquid is cooled and diluted to 200 c.c. (Solution 1). One hundred c.c. of this solution are boiled for 10 minutes after the addition of 0·28 grms. of pure molybdenum metal powder, cooled and diluted to 100 c.c. (Solution 2). The "molybdenum-blue" reagent is made by mixing solutions 1 and 2 in such a proportion that 2·51 c.c. of the mixture will just decolorise $0·20 \pm 0·01$ c.c. of 0·1 *N* permanganate solution. *Method.*—One to 30 c.c. of the solution to be tested (containing 0·0005 to 0·5 mgrm. of P_2O_5 or As_2O_5) are placed in a small 50 c.c. conical flask, neutralised with dilute soda solution or sulphuric acid, 2 drops of saturated aqueous 1, 2, 6-dinitrophenol being used as indicator (slight yellow colour at end-point), diluted to 40 c.c., and the "molybdenum-blue" reagent is added. The solution is boiled gently for 5 minutes, kept for a further 15 to 20 minutes, cooled and diluted to 50 c.c. The intensity of the blue colour is compared with that of a standard phosphate solution, prepared from potassium dihydrogen phosphate, which has been treated in the same manner. The quantity of "molybdenum-blue" reagent to be added depends on the amount of phosphate present, and must be established by preliminary trial: for 0·0005 to 0·1 mgrm. of P_2O_5, 0·3 c.c., and for 0·1 to 0·5 mgrm. of P_2O_5, 0·6 c.c., is required. Various colorimeters are recommended for the colorimetric comparison, but for approximate results a colorimeter is not necessary. Arsenic acid reacts with the reagent similarly to phosphoric acid, and may be determined in the same way, a standard comparison solution prepared from arsenic acid being used. Silica does not interfere. S. G. C.

Micro Melting-Point Determinations. H. Linser. (*Mikrochem.*, 1931, **9**, 255–268.)—Klein's melting-point apparatus (*Mikrochem. Pregl-Festschrift*, 1929, 192) for the observation of melting points under the microscope is used to determine the temperature of sublimation, melting point, temperature of decomposition and other properties of a number of substances. Before use, a new instrument must be heated several times to 400° C., and maintained at that temperature, so that all the insulating material is thoroughly dried, before reproducible results are obtainable. A calibration curve should be made for each instrument by determining the readings for a number of test substances of known m.pt., when heated at a velocity of 3 to 6° per minute. The m.pt. is taken as the temperature at which the smallest crystals and particles liquefy and the corners of the larger crystals begin to melt. This is not necessarily the same temperature as the macro m.pt. The observed m.pt. is lowered by increasing the velocity of heating. For a number of substances it was found that $y = 3·1x$, where x represents melting-point displacement and y the velocity in degrees per minute. Therefore, the velocity

of heating should be observed and the correction applied. A further correction table is advisable, in which the corrected value of the melting points of a number of substances is compared with the known value of their melting points. For most instruments this last correction table is redundant, and the true and calculated values coincide. J. W. B.

Reviews

THE NEW CONCEPTIONS OF MATTER. By C. G. DARWIN, M.A., F.R.S. Pp. 192. London: G. Bell & Sons, Ltd. 1931. Price 10s. 6d.

Although Professor Darwin points out that the methods of analytical chemistry —"heating, dissolving and so on—are much too gentle to do more than scrape the surface of the very stable structure of the atom," yet no chemist, be he analytical or of any other variety, can fail to be interested in recent work on the nature of the different atoms with which he is constantly dealing. Professor Darwin's book is the most successful exposition of the new conceptions of matter that has yet appeared. Starting with an admirably lucid description of the behaviour of particles, continuing with an equally straightforward account of the behaviour of waves, it leads on finally to the evidence which proves that electrons, protons and photons all partake of the nature of particles, and yet also all partake of the nature of waves. The reader is led up to this apparent paradox so deftly that he finds himself happily at home among the new conceptions before he has had time to realise the difficulties of crossing from the old, and the present reviewer, at least, is grateful to the author for having exorcised that paralysing inferiority complex which used to inhibit all mental processes when mathematicians or physicists began to talk about 6-dimensional space. D. JORDAN LLOYD.

ANALYTICAL CHEMISTRY. A Textbook for a One-Year Combination Course in Qualitative and Quantitative Analysis. By JOHN C. WARE, Sc.M., Ph.D., Associate Professor of Chemistry, New York University. Pp. xiv+462. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1931. Price 22s. 3d. net.

Judged by the Table of Contents, this is an attractive book, for it comprises in one volume the fundamental physico-chemical facts and theories underlying analytical chemistry (105 pages), qualitative analysis (158 pages), and gravimetric and volumetric methods (157 pages).

Upon closer acquaintance, however, the book proves to be designed for piloting students in American colleges through a one-year's "pre-medical and pre-dental course" in analytical chemistry. Whilst serviceable to those who desire to get through a subsidiary subject with a certain amount of hustle, if necessary, the book can hardly be said to be of general interest to the analytical profession. This is said without intention to criticise the reliability of the text-matter; it is the recurring *Leitmotiv* of cramming that calls for comment. It is

"not possible in a one-year course to devote much time, if any, to the non-metals" (p. 243). The chapter on the analysis of solids "should, at least, be carefully read through where there is not sufficient time to make the analyses" (p. 233). In the chapter on the "Colloidal State," it is "not possible to go into details as to what really constitutes the colloidal state," but the student will gather the impression that it constitutes a nuisance which should be prevented rather than studied: "Prevention is better than a cure"; in carrying out a precipitation, "the steps must be followed exactly as given." "Accept your procedure instructions as the accumulated experience of many others." W. R. SCHOELLER.

MICROBES AND ULTRAMICROBES. By A. D. GARDNER, M.A., D.M., F.R.C.S. With an Appendix by G. R. DE BEER, M.A., B.Sc. 21 Illustrations. Monographs on Biological Subjects. London: Methuen. Price 3s. 6d.

There are few analysts who do not, at some time or other, find themselves faced with problems in whose solutions a knowledge of bacteriology must play a part. For some, in the food and agricultural trades, for example, this part will generally be of such importance that they themselves will, in fact, not be expected to tackle the problems, since all the larger organisations will include at least one bacteriologist on their scientific staffs. For others the occasions will be so rare, as in the paint industry or in metallurgical work, that recourse to a library or to the services of a less specialised consultant, will doubtless meet the situation. Intermediate between these two groups stand probably most analytical chemists, including those in general practice, to whom at any moment a general knowledge of the methods of bacteriology and the significance of its results may prove essential.

Bacteriology is, fortunately, a subject whose scope and achievements are quite easy to expound even to a non-technical audience, and, *a fortiori*, to chemists. Its technique, on the other hand, is certainly one of the most exacting in the whole realm of science. For that reason, if for no other, scientists working on subjects adjacent to bacteriology need to know what it does, rather than how it does it, and Dr. Gardner's little book seems ideally suited to telling them. It is clearly written; indeed, it is not exaggerating to say that it is extremely well written, with an attention to the exactness and niceties of scientific prose that is usually all too lacking. It covers the whole general field of bacteriology, with special attention to recent developments in the study of viruses—or ultra-microbes, as the author prefers to call them—and the bacteriophage, the latter at perhaps rather disproportionate length. The fundamental facts in the extremely difficult branch of immunology are also given, and the most recent attempt to place bacteriological classification on a sound taxonomic basis is outlined.

Every chemist, particularly every analytical chemist, who is himself not a trained or practising bacteriologist, would be well advised to read this book. If it does not, and it does not set out to do so, teach him bacteriology, at any rate it shows him where he must submit to be taught. No one can read of the problems involved in ultra-microbiology without a realisation of the extreme technical difficulties involved in their solution; no one is likely to tackle them, or other

bacteriological work, after reading Mr. Gardner's book, unless he is satisfied that he has the necessary training and experience.

It is certain, however, that the book will reach a much larger public than the restricted one we have been discussing. Many students will find it a welcome introduction to a frequent subsidiary subject. Consequently, we may be permitted to draw attention to some small defects. The excessive use of diagrammatic illustrations, rather crudely hand-drawn, seems a little out of place in a "Monograph"; occasionally, as in the drawing of *Corynebacterium* (Fig. 2), the effect is so unlike what is actually seen under the microscope as to be actually misleading, but the use of half-tone reproductions of photomicrographs was probably made impossible on economic grounds, because of the low published price of the books in the series.

It would be interesting to learn Dr. Gardner's theories about the facts first made generally known by Besredka, and given by him the most unfortunate and misleading name of "antivirus" phenomena. There is increasing clinical evidence of their importance and quite wide application, and Dr. Gardner goes very near to mentioning them on p. 13, when discussing the possibility that food-exhaustion in a medium can be responsible for the retardation of growth that occurs after the logarithmic phase. If the whole process of culturing, filtering, and sterilisation is repeated a second and a third time, the resulting medium will not support growth of the particular organism that helped to produce it. The dry matter obtained on evaporation of this spent medium can be redissolved to give a medium similarly inhibitory to the relevant organism, and yet able to support the growth of many other species. We can, however, find no explanation of the phenomena in the production by the organism of labile or volatile products toxic to itself.

Attention may, perhaps, be drawn to a few minor blemishes in the author's generally impeccable style; the use of the offensive word "researchers," and of the pointless cliché, "the exception that proves the rule"—especially as the particular exception does not, in fact, prove (that is, *test*) the particular rule—and an over-indulgence in capitals (for example, Hydrogen-ion concentration, p. 41; Mannite, p. 27), might well have been avoided. But, apart from these and an occasional "literal," there are not even minor blemishes to be found in an almost wholly excellent book, a credit alike to author, editor, and publisher.

A. L. BACHARACH.
R. F. HUNWICKE.

QUANTITATIVE ANALYTISCHE MIKROMETHODEN DER ORGANISCHEN CHEMIE IN VERGLEICHENDER DARSTELLUNG. By C. WEYGAND. Pp. 279, with 79 illustrations. Leipzig: Akademische Verlagsgesellschaft, M.B.H. 1931. Price RM. 16, bound RM.18.

The author of a new book on quantitative organic micro-analysis must expect the reader to compare it closely with Pregl's most excellent book on the subject, in order to discover whether the new publication is justified. Professor Weygand has had eight years' experience of teaching and practising micro methods in the University of Leipzig, and has used not only the Pregl methods, but also a number of

other micro- and semi-micro methods, which he describes in his book, with critical remarks on each method. Pregl's book, *Quantitative Organic Micro-analysis*, deals, almost exclusively, with his own methods and those worked out in his laboratory, and gives only brief references to other work; therefore, a book which includes, for the first time, a comparative account of all the different micro methods which have developed from the original Pregl methods, is definitely to be welcomed. The new matter not previously in text-book forms occupies approximately one-half of the book.

Professor Weygand, like Pregl, writes with great attention to detail, which is all-important in micro methods, and his book is intended to be read rather than used as a book of reference. One-third of it is taken up with the description of the determination of carbon and hydrogen by the combustion method. The unchanged Pregl procedure is carefully described, without any historical introduction. Among the slight variations in the Pregl method used by different workers, no mention is made of the use of phosphorus pentoxide as a drying agent in the water-absorption tube. The only reference to the use of phosphorus pentoxide is in the description of a recent semi-micro method, in which it is used with sodium hydroxide as the carbon dioxide absorbent; it was, however, used previously, mixed with glass wool, by Drew and Porter (*J. Soc. Chem. Ind.*, 1928, **47**, 17T) with the otherwise unaltered Pregl procedure, and has been found by a number of workers in England, including the reviewer, and also in Germany, to give much more reliable results, at any rate in a humid climate, than calcium chloride, while it has the advantage that the tubes do not need filling so often.

In the description of semi-micro methods of carbon and hydrogen determination no mention is made of the method for the simultaneous determination of carbon, hydrogen and nitrogen by Hackspill and d'Huart (*Bull. Soc. Chim.*, 1924, **35**, 801; ANALYST, 1924, **49**, 447; and *Recent Advances in Analytical Chemistry*, Vol. II, p. 367). Apart from these omissions, the section is admirably complete, and is a reliable guide to the relative importance of the methods.

Useful additions include Van Slyke's method for the determination of amino nitrogen, the new method of Lieb and Krainick for the micro-determination of carbon by the wet method (*cf.* ANALYST, 1932, 273), and the determination of hydroxyl groups by Flaschenträger.

The book is readable, and well printed and illustrated. It is questionable, however, whether some of the photographs are as useful as they are decorative, since they show very simple details of technique. It is to be regretted that Professor Weygand has not, like Pregl, given a calculation for a typical analysis at the end of each description.

The index, like those of many German books, is inadequate, and this makes the work somewhat difficult to use for reference until one is familiar with the whole of its contents. The book is to be recommended to analytical chemists interested in micro methods, not to replace, but to supplement, Pregl's book.

J. W. BROWN.