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New Processes for the Determination of Traces of Certain Impurities in Lead.*

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

(*Read at the Meeting, May* 4, 1927.)

On account of the extraordinary purity of commercial lead the standard methods of analysis, whilst giving accurate results, are very tedious and cumbersome, and require very large samples (100 grms., at least); also, where it is required to determine a single impurity, a great part of the total procedure has still to be gone through in order to separate it. The object of this investigation was to provide reasonably quick and accurate methods for determining traces of antimony, arsenic, tin, bismuth and sulphur on separate samples of, say, 20 grms. weight or under.

Antimony.—The method is a slight modification of that published by the author for the determination of antimony in copper (Analyst, 1922, **47**, 1). A 20 grm. sample is dissolved in 100 c.c. of nitric acid (sp. gr. 1·2); it is then diluted until all the lead nitrate dissolves, and 80 c.c. of dilute sulphuric acid (1:3) are added; it is cooled and filtered through pulp, the precipitate being washed once or twice with dilute sulphuric acid. The filtrate and washings are evaporated till the sulphuric acid fumes strongly, the residue cooled, taken up with 100 c.c. of water and 50 c.c. of strong hydrochloric acid, and about 5 grms. of sodium hypophosphite are added. The solution is then boiled for about 15 minutes, cooled, 10 c.c. of benzene added, and the whole well shaken and filtered through a wet filter, which is afterwards washed two or three times with hot water. If any notable amount of arsenic precipitates under this treatment, it may be necessary to add more sodium hypophosphite and repeat the process, to ensure all arsenic

* Communication from the Research Department, Woolwich.

being removed. The filtrate and washings are boiled for 1½ to 2 hours (not longer) with a copper strip (about 15 × 1·5 cm.) which has been rolled into an open flat spiral and cleaned with dilute nitric acid. The solution is then poured off, and the copper rapidly washed with cold water, placed in a small beaker of diameter only slightly greater than that of the coil, covered with cold water and about 1 grm. of sodium peroxide immediately added. The operations, from the washing of the coil up to the addition of the peroxide, must be done as rapidly as possible, otherwise the antimony may become insoluble. After standing for five minutes or so the beaker is put on the hot plate and warmed until the copper darkens all over, the liquid is then poured off into a small flask, and the copper and beaker rinsed in twice with distilled water. This liquid should now contain all the antimony in the sample; about 1 grm. of zinc sulphide is added to it, and it is allowed to stand, with occasional shaking, for some hours, preferably overnight. It is filtered through pulp and washed with tap water (from this point forward tap water is used instead of distilled water, which is liable to contain traces of metals which will give colorations with hydrogen sulphide). The filtrate and washings are acidified with 5 c.c. of hydrochloric acid, sulphur dioxide is passed into it for two or three minutes, and the solution is boiled down to about 20 c.c.; it is then cooled, 5 c.c. of 1 per cent. gum arabic solution are added, and the whole is made up to 100 c.c. with tap water. The standard is prepared by adding 5 c.c. of the gum arabic solution and 5 c.c. of hydrochloric acid to 5 c.c. of a solution containing 0·01 per cent. of antimony, and making up to 100 c.c. with tap water. Hydrogen sulphide is passed for about 1 minute through both solutions, which are then poured into Nessler glasses, and their colours matched. This is done by pouring liquid out of the one having the darker tint until the colours match, and then measuring the depths of liquid in the two glasses. If a is the depth of the sample solution, and b the depth of the standard, then $b/a \times 0{\cdot}0005$ = weight of antimony in the sample taken.

The following results were obtained with a sample of lead to which varying amounts of antimony had been added:

Lead taken. Grms.	Antimony added.		Colorimetric reading.	Antimony found.	Antimony recovered.	
	Grm.	Per Cent.		Grm.	Grm.	Per Cent.
20·0	blank	—	72/100	0·00036	—	—
20·0	0·00025	0·00125	104/85	0·00061	0·00025	0·00125
20·0	0·00050	0·00250	104/60	0·00087	0·00051	0·00255
20·0	0·00100	0·00500	104/39	0·00134	0·00098	0·00490

ARSENIC.—A 20 grm. sample is dissolved in 100 c.c. of nitric acid (sp. gr. 1·2), and the process described above for antimony is then followed up to the point of the filtration of the arsenic mixed with benzene; it is, however, desirable to add a second quantity of sodium hypophosphite about ten minutes after the first. The filtrate should be quite bright. The filter containing the benzene suspension of arsenic is washed several times with hot water, the funnel then transferred to a clean flask, the filter punctured with a pointed rod, and the benzene allowed

to run into the flask. The arsenic is washed through into the flask as completely as possible with a jet of cold water, and a measured excess of $N/100$ iodine solution is run slowly over the filter and the sides of the funnel in such a way as to dissolve all remaining arsenic. The funnel and filter are then washed with cold water until all iodine is transferred to the flask, the washing being completed by opening out the paper and rinsing off any drops of benzene that may still cling to it. The flask should now contain all the arsenic in the original sample dissolved in a measured excess of iodine, according to the equation—

$$2As + 5I_2 + 5H_2O = As_2O_5 + 10HI.$$

About 5 grms. of sodium bicarbonate and 2 grms. of potassium iodide are added, and the excess iodine back-titrated with $N/100$ arsenious oxide starch as indicator. The difference between this figure and the titration value of the amount of iodine taken gives the number of c.c. of $N/100$ iodine required to oxidise the arsenic; this figure, multiplied by 0·00015, gives the weight of arsenic in the sample taken.

The following results were obtained with a sample of lead to which varying amounts of arsenic had been added:

Lead taken. Grms.	Arsenic added. Grm.	Arsenic added. Per Cent.	Titration $N/100$ As_4O_6. C.c.	Arsenic recovered. Grm.	Arsenic recovered. Per Cent.
20·0	blank		No precipitate with hypophosphite		
20·0	0·000375	0·0018	24·2 21·2 3·0	0·00045	0·0023
20·0	0·000375	0·0018	24·5 22·0 2·5	0·00038	0·0018
20·0	0·000750	0·0038	24·2 19·1 5·1	0·00076	0·0038
20·0	0·000750	0·0038	24·7 19·7 5·0	0·00075	0·0038
20·0	0·00150	0·0075	24·2 14·7 9·5	0·00143	0·0072

The hypophosphite precipitation of arsenic was first described by Thiele (*Annalen*, 1890, **263**, 361–376); it was further elaborated by Bougault for determining arsenic in cacodylic acid (*J. Pharm. Chim.*, 1909, 13–20). In view of

certain statements in the literature dealing with the precautions necessary to ensure complete precipitation of the arsenic, it is, perhaps, desirable to put on record the results of some experiments carried out to justify the extremely simple procedure described above. Measured amounts of $N/100$ As_4O_6 were placed in flasks with 100 c.c. of water and 100 c.c. of arsenic-free hydrochloric acid, about 10 grms. of sodium hypophosphite were added to each, and all were allowed to stand for ten minutes; they were then put on the hot plate and boiled for fifteen minutes, after which they were cooled somewhat, benzene was added, and they were well shaken and filtered, and the remainder of the process described above was carried out.

The following results were obtained:

No. of c.c. $N/100$ As_4O_6 taken.	Back titration c.c. $N/100$ As_4O_6.	Difference	= No. of c.c. $N/100$ As_4O_6 recovered.
1·0	14·3 − 11·3	3·0	1·2
2·0	14·3 − 10·1	4·2	1·7
3·0	23·8 − 16·1	7·7	3·1
4·0	23·8 − 14·3	9·5	3·8
5·0	23·8 − 11·3	12·5	5·0
6·0	23·8 − 9·6	14·2	5·7
10·0	47·1 − 22·8	24·3	9·8

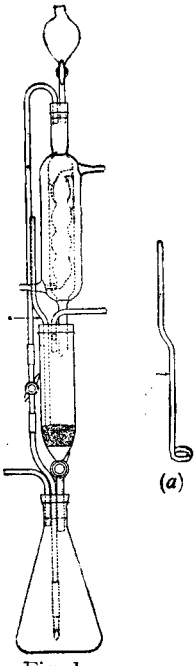


Fig. 1.

These figures show that, for practical purposes, shaking with benzene removes the whole of the arsenic from its colloidal suspension, and renders the prolonged standing recommended by some authors unnecessary.

TIN.—In determining the amount of tin in a sample of lead, containing, say, 1 or 2 per cent., a satisfactory procedure is to dissolve 1 or 2 grms. in hydrochloric acid and bromine, dilute, reduce the tin to stannous condition by, *e.g.* boiling with a coil of lead, and to titrate with iodine. The principal reason why this cannot be applied to small amounts of tin lies in the fact that, owing to the crystallisation of lead chloride, the time taken to dissolve the lead increases very rapidly with the weight of sample taken; consequently, where a 2 grm. sample is a feasible (though somewhat slow) process, a 4 grm. sample already uses more time than is practicable, and a 20 grm. sample would, probably, never dissolve at all. The problem of the solution of large quantities of lead in hydrochloric acid was solved by making use of the very different solubilities of lead chloride in hot and cold aqueous media. The apparatus used is shown in Fig. 1; it consists essentially of the percolator described by the author (ANALYST, 1926, **41**, 229), but contains, in addition, an upright condenser at the top of the main funnel. The return tube is carried to the top of this condenser, to which also the small tapped funnel is transferred; a paper pulp filter is placed in the bottom of the main funnel. The flask contains 20 grms. of the sample, as finely divided as is convenient, together

with 100 c.c. of hydrochloric acid and about 2 c.c. of bromine. About 50 c.c. (or as much as is convenient) of dilute hydrochloric acid (1:1) are run into the main funnel, and, after the percolator has been started, the liquid in the flask is heated by a burner and kept just below boiling point. The lead is attacked, forming lead chloride which dissolves in the hot acid; this hot solution is carried up the return tube, and passing through the condenser, is cooled before reaching the main funnel. When it becomes sufficiently saturated this cooling causes lead chloride to crystallise out, and these crystals are retained on the pulp filter, the liquid returning to the flask being only the cold saturated solution of lead chloride. In this way the lead chloride is continuously removed, and is unable to form a protective layer on the lead. As the bromine is used up, more is added, a few drops at a time, through the top funnel. In practice, it is desirable to add two other features to the apparatus:

(*a*) In view of the increased height of the percolator, owing to the presence of the condenser, there is a distinct tendency for air to be sucked up through the main funnel, thus upsetting the pulp filter. This is counteracted by a glass rod bent at one end into a small ring at right angles to its length; this ring presses on the pulp filter, and the other end passes through the cork which carries the condenser, thus holding the filter firmly in place. This rod is shown both separately and in position ("*a*," Fig. 1).

(*b*) As stannic chloride is somewhat volatile, it is as well to insert a wash bottle (not shown), containing water, between the percolator and the filter pump, the contents of which are added to the main bulk when solution is complete.

Where samples smaller than 20 grms. are used it would probably hasten matters to put a layer of lead chloride crystals on the filter before starting, as there appears to be a considerable tendency to super-saturation, which is apt to delay the initial crystallisation.

With the use of this method the average time of solution of 20 grm. samples of lead in the form of filings would appear to be about 4 or 5 hours, though in one case solution was complete in 90 minutes. To test an extreme case, a single lump of lead, weighing 11 grms., was dissolved; solution was complete in 4 hours, and this time would probably have been reduced by putting lead chloride crystals on the filter.

When solution is complete the apparatus is allowed to run for a further 10 or 15 minutes, to clear out the lead chloride as completely as possible; the burner is then removed, and the percolation continued until the apparatus is quite cold, after which it is disconnected, the contents of the washing bottle poured through the filter into the flask, and the filter washed once or twice with a little cold dilute hydrochloric acid. The tin should now be completely in the solution, the great bulk of the lead being on the filter, although there are generally a few crystals of lead chloride which have been washed through the filter; these are removed by filtering the liquid into a 750 c.c. flask and washing very lightly. To this solution are now added 50 c.c. of strong hydrochloric acid, about 2 grms. of potassium

iodide and a strip of platinum foil, the flask is placed in a cooling bath, about 20 grms. of granulated zinc are dropped in, and the mouth immediately closed with a three-holed rubber stopper carrying the following attachments (Fig. 2):—(*a*) leading tube, from a Kipp's apparatus, delivering CO_2, passing down to about $\frac{1}{2}$ inch above the surface of the liquid; (*b*) small tapped funnel with its stem bent twice so that the bulb of the funnel clears the top of the rubber stopper (to allow of a burette being subsequently inserted in the third hole); (*c*) a removable glass plug.

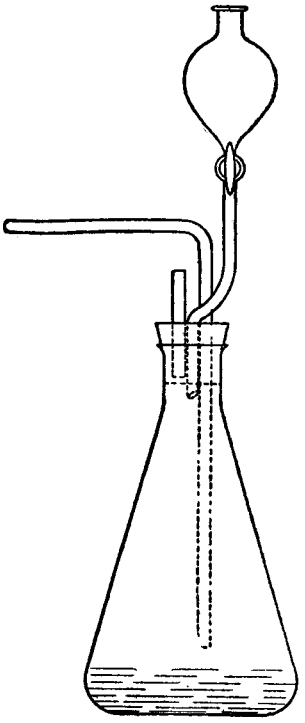


Fig. 2.

The tap of the funnel is opened and the carbon dioxide turned on in a steady stream. When the zinc has nearly all dissolved, the flask is placed on a tripod and the solution boiled (the carbon dioxide current still running) till all the spongy metal, etc., has dissolved. The tap of the funnel is then closed, the flask being simultaneously removed from the tripod and the tap of the carbon dioxide being left open; the flask is then allowed to cool under pressure of the Kipp's apparatus. About 10 c.c. of starch solution are placed in the tapped funnel, the glass plug is withdrawn from the hole in the stopper, and the starch solution is run into the flask, care being taken not to allow the surface to go below the tap; the tip of a burette filled with $N/100$ iodine solution is pushed through the hole formerly occupied by the glass plug. (The jet of this burette must be long enough to allow of its passing completely through the stopper.) The solution can now be titrated with the iodine solution in the burette in complete absence of air.

1·0 c.c. of $N/100$ iodine = 0·000594 grm. of tin.

Trials were made of the efficiency of the reduction and titration, varying amounts of standard stannic chloride solution being made strongly acid and reduced, as above, with zinc in the presence of platinum foil. The following results were obtained:

Tin added. Grm.	No. of c.c. $N/100$ iodine required.	Tin recovered. Grm.
0·0010	1·50	0·0009
0·0020	3·15	0·0019
0·0030	4·90	0·0029
0·0050	7·70	0·0046

The function of the platinum foil is not clear; it is possible that the platinum saturated by the hydrogen generated by the zinc is a more efficient reducer than the zinc itself. It was found, however, that without it the reduction was partial

and unreliable; other authors seem to have had the same trouble with zinc reduction (*cf.* Sandved, ANALYST, 1927, 2, and the various authors he cites).

The complete process was tested on a sample of lead to which varying amounts of tin had been added.

Lead taken. Grms.	Tin added. Grm.	No. of c.c. $N/100$ iodine required.	Tin found. Grm.	Per cent. of tin added.	Per cent. of tin recovered.
20·0	blank	Over-titrated with 2 drops	Nil	—	Nil
20·0	0·0010	1·70	0·0010	0·005	0·005
20·0	0·0020	3·20	0·0019	0·010	0·010
20·0	0·0050	8·10	0·0048	0·025	0·024
20·0	0·0100	15·70	0·0093	0·050	0·047

The following two processes, though only slight modifications of existing methods, are included on account of the tests made of their accuracy.

BISMUTH.—A 5 grm. sample is dissolved in nitric acid (sp. gr. 1·2), the bulk of the nitric acid is evaporated off, and the residue is taken up with water and boiled till all the lead nitrate is dissolved; 50 c.c. of hydrochloric acid are then added and the liquid again boiled, after which it is allowed to cool completely. The precipitated lead chloride is filtered off and lightly washed with cold water. The filtrate is then boiled down to fairly low bulk and cooled, 20 c.c. of dilute sulphuric acid (1:3) are added, and, after standing for a few minutes, the lead sulphate is filtered off and washed two or three times with dilute (about 5 per cent.) sulphuric acid. The filtrate is evaporated and heated till all nitric and hydrochloric acids are driven off, and the residue, after cooling, is taken up with about 50 c.c. of water, boiled, cooled and transferred (if necessary, filtered) into a Nessler glass. The bismuth is then determined colorimetrically with potassium iodide in the usual way.

The following test was carried out:—

Lead taken. Grms.	Bismuth added. Grm.	No. of c.c. Bi solution (1·0 c.c. = ·0001 Bi) required to match.	Bismuth found. Grm.	Per Cent. of Bismuth. added.	Per Cent. of Bismuth. recovered.
5·0	blank	0·7	0·00007	—	—
5·0	0·0010	10·7	0·00107	0·020	0·020

SULPHUR.—A 5 grm. sample in the form of fine shavings is treated with a mixture of 35 c.c. of nitric acid and 25 c.c. of hydrochloric acid and digested on the hot plate till no metallic lead remains; it is then evaporated to dryness, taken up with 25 c.c. of hydrochloric acid and again evaporated to dryness, after which 5 c.c. of hydrochloric acid are added, and then 350 c.c. of hot water, and it is kept boiling till all lead chloride is dissolved. The sulphates present are now precipitated with 20 c.c. of 10 per cent. barium chloride solution, dropped slowly into the boiling solution, and the liquid is allowed to cool and stand overnight. Next day it is digested on the hot plate till all lead chloride has dissolved, it is filtered,

hot (through paper pulp), and the filter washed with boiling water till free from chlorides. The barium sulphate on the filter is burnt off and weighed in the usual way.

The following results were obtained by Mr. S. G. Clarke, who tested the process:

Lead taken. Grms.	Sulphur added as Na_2SO_4		Weight of $BaSO_4$ obtained.		Sulphur recovered.	
	Grm.	Per Cent.	Total.	Net.	Grm.	Per Cent.
5·0	blank		0·0020		—	—
5·0	0·0005	0·010	0·0055	0·0035	0·00048	0·010
5·0	0·0010	0·020	0·0082	0·0062	0·00085	0·017
5·0	0·0015	0·030	0·0120	0·0100	0·00137	0·027
5·0	0·0020	0·040	0·0166	0·0146	0·00200	0·040

A New Method for the Determination of Benzoic Acid in Foods.

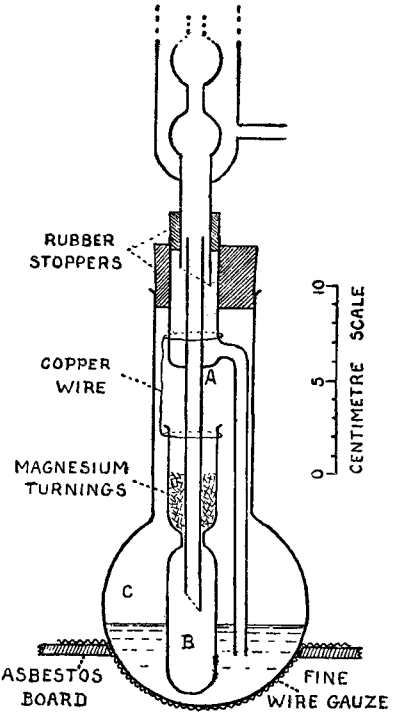
By G. W. MONIER-WILLIAMS, M.A., Ph.D., F.I.C.

In Report No. 39 on Public Health and Medical Subjects, Ministry of Health, 1927 (Analyst, 1927, 153, 229), a method is suggested for the determination of benzoic acid in non-fatty foods, in which advantage is taken of the volatility of this acid in steam from a saturated salt solution. This is due, apparently, to the fact that benzoic acid has a much higher vapour pressure at 109° C. (the boiling point of a saturated salt solution) than at 100° C. (*cf.* N. V. Sidgwick, *Chem. Soc. Trans.*, 1920, **117**, 396). In the method as described the distillate (500 c.c.) is made alkaline and evaporated to a small volume. It is pointed out on pp. 15 and 45 of the above Report that by adopting Wobisch's method of passing the steam through catch-flasks containing sodium hydroxide solution, the evaporation of a large volume of distillate may be avoided, but that this procedure has certain disadvantages, among them being the decomposition of volatile oils, etc., which takes place in the hot alkaline solution.

The following method depends on the observation that when steam containing benzoic acid vapour is passed over moist metallic magnesium in a reflux apparatus, the benzoic acid combines with magnesium to form soluble magnesium benzoate, which can subsequently be extracted by washing the metal with hot water. Since the magnesium never becomes alkaline, decomposition of volatile oils is reduced to a minimum.

The apparatus is shown in the accompanying figure. The glass tube, A, is fitted, as shown, into a rubber stopper, approximately two inches in diameter, which has been bored eccentrically. The tube B, which is constricted in the middle

so as to fit easily over the lower part of A, with a clearance of about 0·5 mm., is fixed in position with copper wire, as shown, and 3 grms. of magnesium turnings (as supplied for Grignard's reaction) placed in its upper part. The magnesium is preferably moistened with a few drops of water. In the flask, C, are placed 50 grms. (or a convenient quantity) of the sample under examination, with about 100 c.c. of water, and common salt is added at the rate of 40 grms. to 100 c.c. of water, the approximate moisture content of the sample being taken into account. The mixture is acidified with about 2 c.c. of syrupy phosphoric acid, and three or four glass beads added to promote regular boiling. These must be larger than the diameter of the return tube, or they may get thrown up into it and block it. The flask is fitted to a good reflux condenser, and the contents boiled rapidly for three hours.



The steam from the flask, carrying with it benzoic acid, passes down through the magnesium, and then up through the inner tube, A, to the condenser. The condensate flows down the inner wall of the wide condenser tube and back to the flask. If a double-surface condenser be used, a small glass cap must be placed over the steam outlet at the top of the tube A, to prevent drops of water from the condenser falling back into the inner tube. The annular space in the upper part of A serves as a trap and prevents the flask contents from being thrown up by steam and air bubbles into the condenser.

During the first few minutes, before the magnesium becomes heated to the temperature of the steam, a certain amount of condensation takes place, and a little water containing magnesium benzoate in solution collects in the lower part of the tube B. Since this part of the tube is immersed in a saturated salt solution, boiling at 109° C., the condensed moisture is soon evaporated to dryness. After the first few minutes the amount of condensation is very slight. At the end of three hours' boiling, the magnesium benzoate formed is found to be partly held by the moist magnesium turnings, either as a solid crust or in aqueous solution, and partly present as a dry residue in the lower part of B.

The apparatus is disconnected and the tube B removed. The magnesium is pushed down with a glass rod into the lower part of B and thoroughly extracted several times with boiling water, being stirred with a glass rod. The success of the determination depends largely on the thoroughness of this extraction. It is best to immerse the tube during this operation in a beaker of boiling water. The

condenser and tube, A, are washed with hot water, and the washings used for extracting the magnesium. The extract is filtered through a small plug of glass wool into a 100 c.c. stoppered cylinder. The colour of the solution varies according to the food under examination. With lemons and tomatoes it is light yellow, but with coffee extract or onions it may be dark brown. It is made strongly alkaline with 20 drops of 40 per cent. sodium hydroxide solution, cooled to 40°–50° C., and oxidised with a saturated aqueous solution of potassium permanganate until the pink colour of the permanganate persists for some minutes. Excess of permanganate is then destroyed with sulphur dioxide or sodium sulphite, and the precipitated manganese dioxide dissolved by adding a few drops of strong sulphuric acid. The liquid, which is usually quite clear and colourless, is then extracted with a mixture of methylated ether and petroleum spirit after saturation with salt, the solvent evaporated, and the benzoic acid sublimed as described in the Report referred to above. The residue before sublimation is almost invariably quite white and crystalline.

The results obtained by this method are given in the table below. It will be seen that, for the most part, they compare well with those given in the Report as having been obtained by steam-distillation and evaporation of the distillate. The method is not suited, however, for foods containing any considerable amount of acetic acid, such as vinegar and pickles, nor did it give satisfactory results in one experiment with salicylic in place of benzoic acid (omitting permanganate oxidation).

In some of the experiments different forms of magnesium were used, with equally good results. Magnesium rod of 4·5 mm. diameter, if cut into small pieces about 4 to 5 mm. in length, has the advantage that it is easily washed, but the amount of surface available is small in proportion to the weight of metal. When in this form the metal can be used over again many times, and the fact that the surface becomes dull and dark grey in colour does not seem to affect its action on benzoic acid. In tests 1, 2, 3, 4, and 10 the same magnesium was used without any treatment other than washing in hot water. Magnesium wire of 1·5 mm. diameter, cut into lengths of 5 to 10 mm. has also been employed with satisfactory results, and may be used repeatedly. On the whole, it saves time and trouble to use fresh magnesium turnings for each determination.

In several of the experiments the mixture was refluxed for two hours only, the results being in most cases the same as with three hours' boiling. In experiment No. 4 two hours' boiling appeared to be insufficient. The time allowed will depend, no doubt, on the rate of boiling, the nature of the food, and possibly the amount of benzoic acid present.

The chief advantages of the method are: (i) that it requires no personal attention during the three hours' boiling, and (ii) that it effects a considerable saving of bench space, a matter of some importance in a small laboratory. In its present form, however, it is not so generally applicable as the steam-distillation method.

No.	Nature of sample and amount taken.	Form of magnesium used.	Duration of boiling. Hours.	Benzoic acid added. Grm.	Weight of residue before sublimation. Grm.	Weight of of sublimate. Grm.
1	Lemon (50 grms.) ..	4·5 mm. rod (bright surface)	2	0·0524	0·0539	0·0499
2	,, ,, ..	,, ,, ,, (dull surface)	3	0·0715	0·0692	0·0663
3	,, ,, ..	,, ,, ,, ,, ,,	3	0·0412	0·0417	0·0392
4	Lemon (50 grms.) + cane sugar (15 grms.) ..	,, ,, ,, ,, ,,	2	0·1378	0·1346	0·1277
5	Lemon (50 grms.) ..	1·5 mm. wire (dull surface)	3	0·1063	0·1073	0·1033
6	,, ,, ..	Bright turnings, 3 grms.	2	0·1054	0·1024	0·0999
7	,, ,, ..	,, ,, 3 ,,	3	0·0359	0·0362	0·0342
8	,, ,, ..	,, ,, 2 ,,	3	0·1112	0·1108	0·1058
9	,, ,, ..	,, ,, 3 ,,	3	Nil	0·0031	0·0016
10	Tomato (50 grms.) ..	4.5 mm. rod (dull surface)	3	0·0822	0·0842	0·0792
11	,, ,, ..	Bright turnings, 3 grms.	2	0·0452	0·0450	0·0432
12	,, ,, ..	,, ,, ,,	3	Nil	0·0034	0·0015
13	Orange (50 grms.) ..	,, ,, ,,	3	0·0641	0·0712	0·0609
14	,, ,, ..	,, ,, ,,	3	Nil	0·0093	0·0032
15	Coffee (30 grms.) + cane sugar (10 grms.) boiled and filtered ..	,, ,, ,,	3	0·0423	—	0·0385
16	Coffee (30 grms.) + cane sugar (10 grms.) boiled and filtered ..	,, ,, ,,	3	0·0291	0·0304	0·0274
17	Coffee (30 grms.) + cane sugar (10 grms.) boiled and filtered ..	,, ,, ,,	3	Nil	0·0050	0·0017
18	Malt vinegar (50 c.c.) ..	,, ,, ,,	3	0·0546	0·0485	—
19	Onions (50 grms.) + vinegar (12 c.c.) ..	,, ,, ,,	3	0·0310	0·0240	—
20	Onions (50 grms.) + vinegar (12 c.c.) ..	,, ,, ,,	3	Nil	0·0030	—
21	Lemon (50 grms.) ..	,, ,, ,,	3	0·0679 (salicylic acid)	0·0603	0·0452

Fresh cherries and strawberries have been tested by a modification of this method, in each case 1200–1500 grms. of the fruit being used in two five-litre flasks and refluxed for 10 to 12 hours. The strawberries yielded 0·002 per cent. (20 parts per million) of a crystalline residue which, on purification, gave the reactions of cinnamic acid. Both fruits showed traces of salicylic acid, which was determined colorimetrically and found to be not more than one part in 20 millions in each case. No benzoic acid could be detected in either of the fruits.

Much of the analytical work for this paper has been carried out by my assistant, Mr. W. A. Godby.

The Application of Ridsdale's Modification of Pemberton's Method for the Volumetric Determination of Phosphoric Anhydride to Fertilisers.

By A. M. CAMERON, B.Sc., F.I.C., and W. T. DOW, A.I.C.

(*Read before the Association of Public Analysts of Scotland.*)

Some time ago the attention of one of us was directed to the method of Ridsdale & Co., of Middlesbrough, for the determination of phosphorus in slag, iron and steel. This is a modification of Pemberton's volumetric method of precipitation of phosphate as ammonium phosphomolybdate, and solution of the precipitate in standard alkali, in which the reagents are added in the form of tablets of constant composition.

It was decided to test the method as applied to the analysis of fertilisers generally, and after various modifications had been tried, the following method was standardised:

The more important of the modifications made were: firstly, the neutralisation of the solution by caustic alkali before acidification to constant strength prior to precipitation. This allows a free hand in the amount of acid used in bringing the phosphate into solution. The sodium nitrate thus introduced does not interfere.

Secondly, use was made of the Leffmann-Beam centrifuge for dealing with the precipitate. This avoids the filtration of more than a small amount of the bulky precipitates dealt with. It should be mentioned that longer buckets than those of the standard apparatus had to be fitted to the machine to hold the Nessler cylinders used.

The method we have found to be accurate and convenient, and worthy of general attention. The following solutions are required:—Nitric acid (sp. gr.1·42), ammonium molybdate (150 grms. p. litre), sodium hydroxide solution (about 30 per cent.), nitric acid (sp. gr. 1·20), potassium permanganate (5 per cent.), and nitromolybdate reagent (prepared by pouring 725 c.c. of the molybdate solution into 275 c.c. of the concentrated nitric acid (1·42). This solution should not be kept more than 10 to 12 days. Ridsdale & Co.'s tablets used are "Analoid" No. 7 (ammonium nitrate 1·75 grms. + ammonium chloride 1·6 grms. + ammonium oxalate 0·25 grm.); and "Analoid" No. 4 ($KmNO_4$ 0·25 grm.). Potassium nitrate (0·1 per cent. solution) is used as wash liquor (Lavol; Analoid No. 14).

Standard solutions:—$N/2$ nitric acid (standardised against sodium carbonate and methyl orange). $N/2$ sodium hydroxide (free from carbonate) prepared by adding a small excess of barium hydroxide to the sodium hydroxide solution,

diluting to required volume and filtering and kept in the usual siphon bottle with soda-lime guard tube.

METHOD OF ANALYSIS. TOTAL PHOSPHATE.—A weighed portion of the sample, the organic matter, if present in material extent, having been destroyed by ignition, is placed in a beaker and boiled with 100 to 150 c.c. of water + 20 to 30 c.c. of concentrated nitric acid. The undissolved matter is allowed to settle, and the liquid decanted into a 500 c.c. flask. The residue is treated with a little water, 8 c.c. of nitric acid and 5 c.c. of concentrated hydrochloric acid, and heated on the sand-bath till oxides of nitrogen and chlorine are no longer evolved. The contents of the beaker are diluted somewhat with water, and the beaker is placed in the water-bath for a few minutes. When cool, the contents are added to the liquid in the 500 c.c. flask, which is made up to the mark with water and filtered.

Twenty-five c.c. of the filtrate are transferred to a 200 c.c. beaker-flask, which is marked at the side at the 60 c.c. level.

Sodium hydroxide solution (30 per cent.) is added, drop by drop, till a permanent precipitate is just obtained. This is re-dissolved by the addition, drop by drop, of nitric acid (sp. gr. 1·20), after which 4 c.c. more of the acid and a few drops of the permanganate solution are added. The solution is warmed, and, if decolorised, more permanganate is added. While still warmed (not boiling), one No. 7 Analoid is added. This decolorises the permanganate. When it has dissolved, the contents of the beaker are diluted to the 60 c.c. mark, the sides of the vessel being washed down.

The liquid is heated to boiling, and when just boiling the beaker is removed from the flame, a rotating motion being given with the hand, and then a mixture of 25 c.c. of molybdic solution + 20 c.c. of water is poured in rapidly (cold) from a Nessler tube. The shaking of the beaker is continued for a minute, and it is then set aside for 10 minutes.

The liquid is decanted through a filter funnel with a short stem containing a small plug of wet cotton-wool. The precipitate is washed with "Lavol" into a Nessler tube of about 65 c.c., which is placed in the bucket of a Leffmann-Beam centrifuge, and whirled for about a minute. The supernatant liquid, which should be quite clear, is decanted off through the funnel (the beaker-flask being rinsed at the same time and the liquid added to that in the funnel), and the funnel washed round with Lavol. The Nessler tube containing the precipitate is nearly filled with the wash liquor, and closed with a rubber stopper bored with one hole. The hole is then filled with a glass plug, and the contents of the tube shaken. The stopper is removed, and the tube filled up with Lavol. It is then again centrifuged. The process is repeated till the precipitate has been washed free of acid, as shown by the addition of a drop or two of dilute methyl orange to the filtrate. As a rule, three or four washings suffice.

The precipitate is washed into the beaker-flask in which the precipitation was made, the cotton-wool added, and the funnel washed clear of any adhering

precipitate. An excess of $N/2$ sodium hydroxide solution is run in. When it is judged that all the yellow precipitate has been dissolved, a few drops of phenolphthalein solution are added, and the excess alkali titrated with $N/2$ HNO_3.

1 c.c. of $N/2$ NaO = 0·001542 grm. P_2O_5.

DETERMINATION OF WATER-SOLUBLE PHOSPHATE.—Twenty-five c.c. (or 10/15 c.c. in the case of a superphosphate) of the water solution obtained by the official method are transferred to the 200 c.c. beaker-flask, a precipitate just produced with the sodium hydroxide solution (one drop as a rule sufficient), and the analysis carried out as above.

CITRIC-SOLUBLE PHOSPHATES.—Twenty-five c.c. of the solution as obtained in the Official Method (0·25 grm. of the original sample), are transferred to the beaker-flask, 6 c.c. of nitric acid (sp. gr. 1·20) are added, and the solution boiled for 5 minutes to effect partial oxidation of the citric acid. The oxidisation is completed by the addition of 3 of the No. 4 "Analoids," as above. The No. 7 tablet is then added, and, when the solution is clear, the solution is diluted to the 60 c.c. mark, and the analysis completed as above.

REMARKS.—The quantity of phosphate taken should be such that the amount of $N/2$ alkali consumed by the yellow precipitate does not much exceed 30 c.c. Most conveniently it should be between 20 and 30 c.c. For example, for a manure with 25 per cent. of total phosphate, a convenient amount is 7·5 grms. of the sample to 500 c.c.

When adding the No. 7 tablet, the solution should not be too hot, or violent effervescence will take place as the permanganate is being decolorised.

It is absolutely essential that the precipitate should settle quite sharply. With a little practice this can usually be ensured. If it does not, it is usually an indication that too much phosphate has been taken. It is futile to attempt to continue with an unsatisfactory precipitate. It must be rejected and the analysis started afresh.

The cotton-wool is prepared by boiling with water, and is kept under water and used wet. The filter funnel is conveniently supported in a tall gas jar. Filtration can be very rapid, and the liquid may be allowed to run through in an almost continuous stream.

Titration should be carried out at about 60° C. The caustic alkali tends to adhere to the cotton wool, and after the addition of the $N/2$ acid to neutrality, it will usually be found that after standing for a minute or so a few more drops of the acid are needed.

A considerable number of analyses having shown the method to be reliable, a series of tests was made between the method and the official gravimetric method. To obviate any possibility of the introduction of errors from difference of apparatus, the same pipettes and graduated flasks were used in each case.

The following results were obtained:—

Nature of Fertiliser.	Ridsdale's modification. Per Cent.	Official method. Per Cent.
Compound manure (total phosphate)	16·98	16·81
(soluble phosphate)	14·94	14·87
Peruvian guano (total phosphate)	21·61	21·56
	21·55	
	21·58	
Compound manure (citric soluble phosphate)	29·60	29·56
Superphosphate (soluble phosphates)	33·00	32·95
Superphosphate (soluble phosphates)	33·04	
Soluble phosphate (supers)	31·32	31·43
Compound manure (total phosphate)	25·28	25·37
Compound manure (total phosphate)	30·10	29·98
Bone meal (total phosphate)	44·51	44·60
Meat-bone meal (total phosphate)	29·24	29·16
Compound manure (total phosphate)	17·77	17·73
Compound manure (citric soluble phosphate)	27·21	27·05

With the exception of the first case, in which the gravimetric precipitate was rather small, these results agree very well. It was found in this series that by using the theoretical factor for the yellow precipitate slightly high results were obtained in the volumetric method. The factor used in the above series is 1 in 338 lower than the theoretical value. Possibly the lowness of results obtained in the gravimetric method that necessitated this correction are due to the slight solubility of the magnesium ammonium phosphate in ammonia, since, to limit errors of weighing, rather large precipitates were dealt with, entailing thorough washing. With the method made standard, it would no doubt be advisable to keep to the theoretical figure.

The effect of the interference of arsenic was examined.

With a sample containing 10 per cent. of arsenious oxide the results were 1 in 70 too high.

With 6 per cent. As_4O_6 1 in 120 too high.
With 3·5 per cent. ,, 1 in 150 ,, ,,
With 2 per cent. ,, 1 in 220 ,, ,,

With this amount of arsenic present in a superphosphate it would mean that the sulphuric acid used in its preparation contained about three times as much. But even the lowest figure would be very rarely met with, and even with impossible amounts of arsenic the error would never become gross. In any case, with the high percentages of arsenic as above, double precipitation of the phosphate would probably be necessary with the Official gravimetric method to ensure accuracy, and this is not provided for in the Official Method under the Fertilisers and Feeding Stuffs (Methods of Analysis), 1908.

NOTE.—Richards and Godden (ANALYST, 1924, **49**, 565), working on Neumann's modification of the volumetric phospho-molybdate method failed to obtain concordant results. Neumann dissolves the yellow precipitate in an excess of standard

alkali, boils to expel ammonia, and, when cold, titrates back the excess alkali with standard acid. The authors named found that the alkali, after being boiled, absorbed carbon dioxide, and hence their results varied according to the excess of alkali taken. To obviate this source of error, they added excess of standard acid, after first boiling off the excess of ammonia, then boiled to get rid of carbon dioxide, and titrated the solution, after cooling, with standard alkali. By this means they obtained satisfactory results.

It should be explained that when using Ridsdale's method this procedure is unnecessary, as the standard alkali does not absorb a material amount of carbon dioxide unless it has been first boiled. The following figures show this:

Fifteen c.c. alkali ($N/2$) were diluted with 150 c.c. water—

Titrated at once, required 15·04 c.c. $N/2$ nitric acid.

Boiled for 20 minutes and allowed to stand for 55 minutes, 14·29 c.c. $N/2$ nitric acid.

Allowed to stand for 55 minutes without previous boiling, 14·92 c.c. $N/2$ nitric acid.

When using Ridsdale's method the alkaline solution does not need to stand for more than about 2 minutes.

The Sequence of Strokes in Writing.

By C. AINSWORTH MITCHELL and T. J. WARD.

(*Read at the Meeting, April* 6, 1927.)

The problem of ascertaining which of two portions of writing on a document was written first frequently presents itself and is seldom easy to solve. Occasionally, chemical methods are available, as when the writings are both in iron-gall inks, the chemical changes in which can be followed by corresponding changes in colour, or when the inks in the writings behave differently when tested with chemical reagents. Thus it has been shown by Mitchell (Analyst, 1920, **45**, 247) that it is possible to observe and record the progressive change in colour in a blue-black ink freshly applied to the paper, at first hourly, then day by day, and week by week, and finally month by month, up to a limit which may vary with the conditions from, say, five or six months to about a year. For example, if the writing in an entry upon the page of an account book which purports to be nine months old shows a pronounced change of colour from bright blue to a darker tint in the course of a day or two, whilst the remaining entries show no change in colour

during the period, there can be little doubt that the former was written more recently than the latter.

Or, again, if writing in blue-black ink which purports to be ten years old reacts immediately with dilute hydrochloric acid, the inference is that it is probably not more than three or four years old, at most, since the iron tannate in completely oxidised iron-gall ink on paper is colloidal in character, and protects the soluble blue dye from the action of the reagent. This was the basis of the evidence given in the case of *Rex* v. *Pilcher* (ANALYST, 1920, **45**, 253).

Another possible means of ascertaining the relative ages of two given pieces of writing is to determine the sequence of formation of contiguous characters. This can only be done when certain strokes of the two writings intersect one another; but, given such conditions (which are not of infrequent occurrence), it is obvious that if one can determine with certainty which of two intersecting strokes is uppermost, there can be no doubt which writing is the more recent.

Unfortunately, the appearance of the crossed strokes may sometimes be misleading, and a line which was made prior to a second line may appear to be unmistakably uppermost both under the microscope and in a photomicrograph. In order to discover the conditions under which one can accept ocular evidence on this point as valid, we have made a series of systematic experiments, extending over more than a year, in which we have studied the intersections of strokes made at different periods with pencils of different kinds, and with iron-gall and other types of inks.

GRAPHITE PENCIL STROKES.—It has been shown by Mitchell (*J. Soc. Chem. Ind.*, 1919, **38**, 383T; *Nature*, 1920, **105**, 12; 1922, **109**, 516; ANALYST, 1922, **47**, 379) that natural graphites contain siliceous impurities which appear as disjointed white striations on a dark background of pigment. The old graphite pencils, which were cut from the natural mineral, might be fairly free from these siliceous particles in certain portions, but rich in them in others; hence the possibility of determining which of two strokes made with such pencils was uppermost would depend upon whether the intersecting lines showed a continuous seam of white striations at the point of intersection. For this reason it would not have been possible to apply the test to the lines made with some of the finest graphite pencils from the old Borrowdale mines. This limitation, however, does not apply to the modern blacklead pencils, which contain an artificial pigment largely composed of a mixture of ground graphite and clay. The marks made with these pencils show regular uniform bead-like striations, and when two lines cross one another there can be no doubt as to which is on top.

GRAPHITE PENCILS AND IRON GALL INKS.—A pencil stroke made above an ink stroke can be seen to be uppermost (Fig. 1). Conversely, an ink stroke made above a pencil stroke and allowed to dry usually appears unmistakably on top (Fig. 2), but if the ink stroke has been blotted immediately after its application to the paper, so that most of the iron tannate of the ink has been

removed, leaving mainly the blue dye, it is wiser to express no opinion, unless sufficient pigment has been left to cause a definite break in the striations in the pencil pigment (Fig. 3).

COLOURED PENCILS.—The blue and red pencils in common use generally contain an insoluble pigment which is conveyed to the paper in a wax-like medium. Owing to the pigment being carried in streaks over the paper, it is occasionally easy to decide which of two crossing lines is on top.

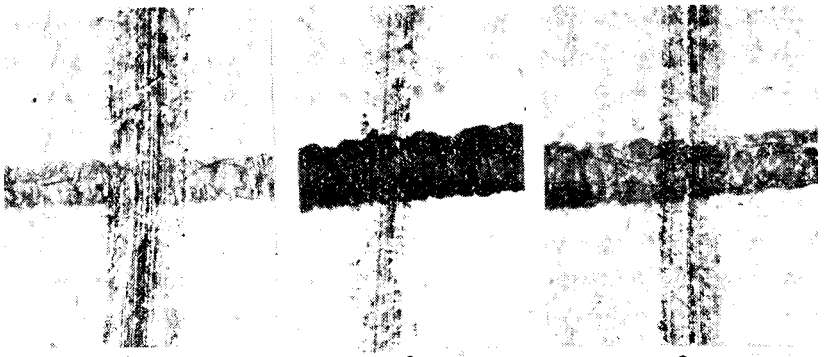
When strokes with a blue or red pencil are made on the top of a blacklead pencil mark the reflection of light by the graphite is usually dimmed at the point of intersection, and there can be no doubt as to the coloured pigment being uppermost. Conversely, when the blacklead pencil marking is on top, the coloured pigments show reflection intensified by the graphite at the crossing. This is very pronounced with some blue pencil markings; less pronounced with red pencil marks. The siliceous striations of the graphite pencil may also afford evidence on the point. When the markings have been made over lines in blue-black ink the appearance of their relative position agrees with the facts, and this also applies to the marks made with blue-black ink on the top of the coloured pencil pigments, provided that the ink was not blotted immediately, in which case the indications will be uncertain. It should be noted, however, that the ink mark is often thinner and ragged where crossing a coloured pencil mark.

COPYING INK PENCILS.—As a rule, it is not possible to determine which stroke is uppermost. This appears to be due to the aniline dye spreading over the interstices between the particles (Fig. 4).

When graphite is a constituent of the composite pigment it is possible to burn away the organic matter, leaving the graphite and the kaolin on a background of the coherent ash of the paper. The continuous striations of the graphite can then be followed, and it can be clearly seen which line is uppermost (Fig. 5) (*cf.* ANALYST, 1925, **50**, 177). When the dye is incorporated in the composite pigment in the form of an alumina lake and no graphite is present this calcination test may fail to give a decisive result.

STAMPING INK.—Stamping inks composed of a solution of an aniline dye in alcohol or water, with a suitable thickening agent, can rarely be distinguished when superimposed on other marks. As a rule, when a stamped impression is put either above or below a pencil or ink marking, it will appear to the eye unmistakably below (Fig. 9). Only when the stamping ink is very concentrated, so that an insoluble layer separates on the surface, is it possible to see the lustre of the solid particles, and thus be in a position to state that the stamping ink is uppermost (Fig. 8). For this purpose approximately vertical illumination is necessary. In one case within our experience a clerk was accused of having falsified a receipt, because the pencil writing appeared obviously to be above the impression of the rubber receipt stamp, and therefore to have been written subsequently. After the fallacy underlying this deduction had been demonstrated the charge was withdrawn.

INTERSECTING LINES MULTIPLIED 13 DIAMETERS.



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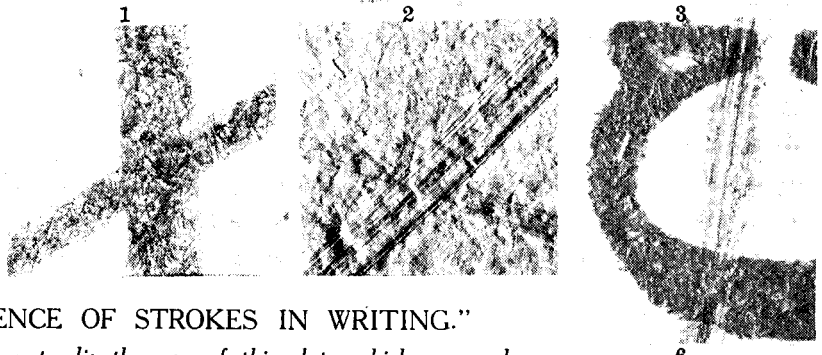

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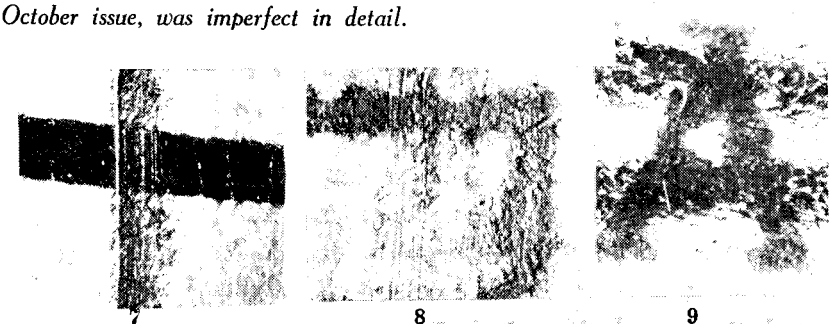
"SEQUENCE OF STROKES IN WRITING."

By an unfortunate slip the copy of this plate, which appeared in the October issue, was imperfect in detail.



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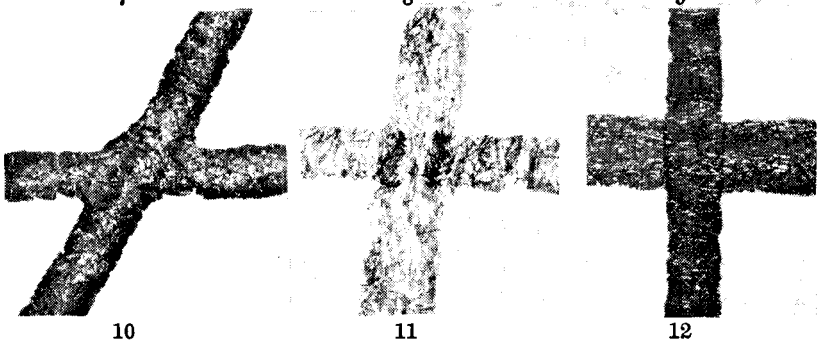

10 11 12

1. Lead pencil on old blue-black ink. 2. Blue-black ink (not blotted) on lead pencil. 3. Blue-black ink (blotted) on lead pencil. 4. Copying ink pencil on copying ink pencil. 5. Copying ink pencil on copying ink pencil, ashed. 6. Printing ink on lead pencil. 7. Lead pencil on artists' black ink. 8. Stamping ink (concentrated) on lead pencil. 9. Carbon copy on stamping ink. 10. Logwood inks strokes (crossed immediately). 11. Blue-black ink on blue-black ink, blotted. 12. Blue-black ink strokes, crossed after 48 hours.

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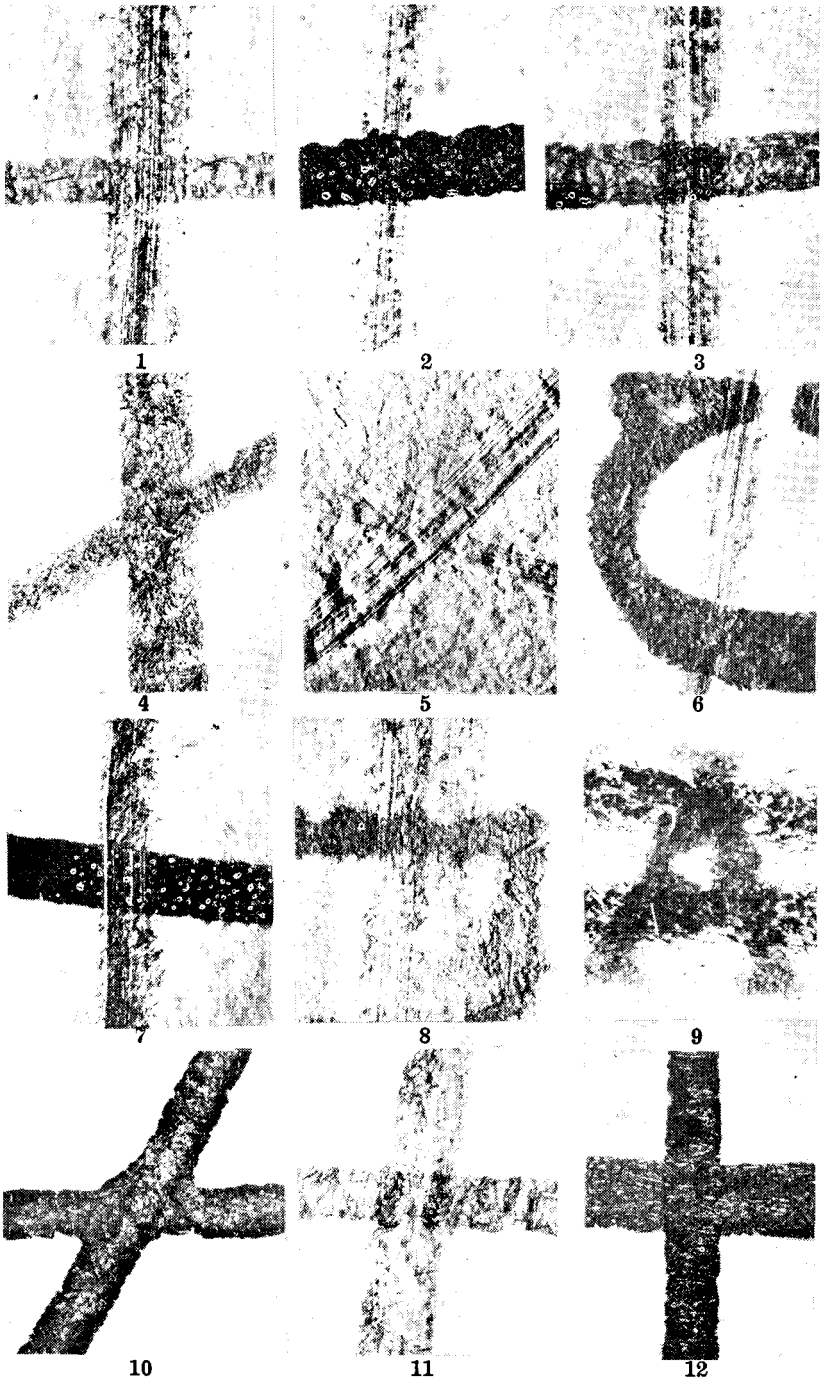

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PRINTING INK.—It is rarely possible to decide as to the relative positions of impressions of printing ink on printing ink. Only when one ink is new and the other old is a relief effect sometimes to be seen.

When pencil markings cross printed impressions it is, as a rule, possible to determine which is uppermost, for, apart from the striations, the pencil may make a groove in the paper, which can be seen by oblique lighting (Fig. 6). Strokes in writing ink made on the top of printed matter can sometimes be seen to be on the top, especially if the writing has not been blotted. In that case there must be uncertainty, unless the pen has been pressed heavily on the paper, so that the nib has left furrows which can be seen to cross over the printed line.

The true position of printing ink marks on a blue-black ink line often appears uncertain, but sometimes may be ascertained.

ARTISTS' BLACK INK.—This usually consists of an insoluble pigment (lamp-black) suspended in a resinous medium. As a rule, it is possible to determine which of two intersecting strokes is uppermost.

Coloured pencil pigments usually form a solid continuous layer, which enables one to decide whether they are above or below the artists' ink. Graphite pencil markings can be followed by their striations (Fig. 7), and the position of strokes in writing ink which has not been blotted can be decided after the ink has dried for some hours.

WRITING INKS.—When two strokes in iron-gall ink, blue-black ink or logwood ink (Fig. 10) are made to intersect one another at short intervals it is seldom possible to decide with certainty which is uppermost. We have made many experiments to determine the period of time which must elapse between the making of the first and of the second stroke before it becomes possible to determine the relative positions of the two. When the second stroke is made three hours after the first the relative thickness of the lines is an important factor in judging at a subsequent period which line was made first. If the uppermost line is a very thick one, there can be no doubt from the appearance that it is on top; but if the top line is only lightly made, the conclusion must be uncertain.

With an interval of seven hours between the strokes there must be uncertainty about the relative position of some of them. With an interval of 24 hours there can be no doubt about heavy lines on thin lines, but one cannot always be certain about thin lines made over heavy lines. With an interval of 48 hours there can be no doubt as to the position of the intersecting strokes, whether the writing is heavy or light (Fig 12).

The principle underlying these facts is that when both lines are freshly applied to the paper the oxidation of the ink proceeds at practically the same rate, and the insoluble iron tannates formed mingle at the point of intersection. When, however, the lower ink has already become partly oxidised, the second ink then forms the insoluble pigment on the top of it without mingling with it, and can thus be seen as a superposed layer. The minimum time required for one to be certain that the mingling of the pigments will not occur, is, as stated above, about 48 hours.

The effect of blotting a freshly written line in blue-black ink is to remove a large proportion of the still soluble iron tannate, leaving blue dye on the paper, together with such a small proportion of the iron pigment that the ink remains semi-transparent on oxidation (Fig 11).

If the first line has been blotted, but the second has not, the insoluble pigment will form on the top of the blotted ink line, and can eventually be clearly distinguished as above it. If, however, the blotted line is uppermost it is usually impossible to determine which of the two lines is above the other, and the deduction becomes uncertain. Hence before coming to a conclusion from the appearance of the lines under the microscope, it is essential to ascertain that neither line has been blotted, or if either line has been blotted some seconds or minutes after its application to the paper, to see that sufficient iron tannate has been left to insure the formation of the insoluble tannate. For this purpose micro-chemical tests may be applied to the inks on the paper by means of a capillary pipette.

Additional evidence may sometimes be obtained by noting the way in which the ink may spread when it crosses a line previously written. While the inks of both lines are still wet the soluble pigments mingle, and occasionally the corners of the angles formed by the intersecting lines become less sharp (Fig. 10). On the other hand, when a second stroke passes over one which is almost dry, the ink may spread upwards and downwards on the first stroke, forming a dark margin on each side of the second stroke. A good example of this spreading is given by Osborn in his book, *Questioned Documents* (p. 379). In our experience this spreading of the ink from the second line along the first may afford valuable information, but the spreading is dependent upon various conditions, such as the characteristics of the inks, the hardness of the surface, the texture of the paper, the angle between the strokes, the amount of ink delivered, and the pressure applied by the pen, and the absence of spreading does not necessarily mean that the two lines were not made at about the same time.

To sum up: When the pigment of the ink is in solution, like the blue dye in a blue-black ink or the dye in coloured writing inks, or in stamping inks, or in certain typing inks, it is more or less transparent, and does not undergo any material physical change on exposure of the paper to the air. In these circumstances differentiation of the sequence of intersecting lines is uncertain. The possibility of deciding which of the two lines is uppermost must depend on either the original presence of an insoluble pigment or the eventual formation of an insoluble pigment from a soluble one.

The Detection of the Prohibited Vegetable and Coal Tar Colours in Foodstuffs.

By JOHN RALPH NICHOLLS, B.Sc., F.I.C.

The Public Health (Preservatives, etc., in Food) Regulations, 1925, prohibit the use in foodstuffs of the vegetable colouring matter, gamboge, and five coal tar colours. The latter are specified in the Regulations as in the first three columns of the following table, the fourth column indicating the chemical name:—

Number in Colour Index of Society of Dyers and Colourists, 1924.	*Name.*	*Synonyms.*	*Chemical name.*
7	Picric acid.	Carbazotic acid.	Trinitrophenol.
8	Victoria yellow.	Saffron substitute; Dinitrocresol.	Salt of *o*- and *p*-dinitrocresols.
9	Manchester yellow.	Naphthol yellow. Martius yellow.	Salt of dinitronaphthol.
12	Aurantia.	Imperial yellow.	Ammonium salt of hexanitrodiphenylamine.
724	Aurine.	Rosolic acid. Yellow coralline.	Mixture of trioxytriphenylcarbinol, oxidised aurine, pseudorosolic acid and their salts.

The object of this investigation was to provide a simple scheme for the ready detection of all the above prohibited colours, which could easily be applied for routine examinations.

Commercial samples of the colours were purchased, but it was found that the one marked "Aurantia" was a sulphonic acid colour, the makers stating that No. 12 of the Colour Index was not on the market at the present time. For the purposes of this investigation Aurantia from a specially prepared specimen of hexanitrodiphenylamine was employed.

Preliminary experiments with the specified colours showed that dyeing tests with wool were useless as a means of detection. The dye solutions were only deeply coloured when alkaline, acidification producing colourless solutions or giving yellow precipitates according to their strengths. Wool could not be dyed

(*Continued on page* 588.)

SUPPLEMENTARY TESTS

	Tests on dilute soda solutions obtained in scheme for detection of prohibited dyes.	*Picric acid.* *Trinitrophenol.*	*Victoria yellow.* *Dinitrocresol (o- and -p).*	*Naphthol yellow.* *Dinitronaphthol.*	*Aurantia.* *Hexanitrodiphenylamine.*	*Aurine.* *Trihydroxytriphenylmethane.*	*Gamboge.*
(1)	Melting point of ethereal extract from acid soln. (from literature).	121°–122·5° C.	85°–86° C., or 80·5° C.	138° C.	238° C., with decomp.	not melted at 220° C.	75°–80° C.
(2)	Colour of weakly alkaline solution: Strong in colour.	yellow	orange yellow	orange yellow	orange red	red	orange red
	Weak in colour.	yellow	yellow	yellow	orange yellow	red	yellow
(3)	Taste of soln. diluted till almost colourless.	bitter	——	——	——	——	——
(4)	Strong soda added to alkaline soln.	deepens considerably	no change	no change	reddens slightly	no change	slightly turbid
(5)	Excess of salt added to alkaline soln.	no change	no change	no change	no change	no change	soda salt thrown out as reddish yellow ppt.
(6)	Dilute acid added to alkaline soln.: Strong.	no change	yellow ppt.	yellow ppt.	yellow ppt	yellow ppt.	yellow ppt. which on boiling collects as brown drops
	Weak.	no change	colourless	colourless	colourless	yellow soln.	colourless
(7)	To 1 vol. add 10 vols. concentrated sulphuric acid.	colourless	colourless	faint yellow	faint yellow	yellow	brownish
(8)	Alk. soln. boiled with ammonium sulphide.	deep reddish brown	faint reddish brown	faint reddish brown	deep brown	no change	no change
(9)	Alk. soln. boiled with KCN.	do.	deepens to orange brown	deepens	dull brown	slowly discoloured	do.
(10)	Acid soln. boiled with $SnCl_2$.	decolorised	decolorised	decolorised	yellowish brown to deep reddish brown.	no change	do.
(11)	Boiled with zinc dust and ammonia.	deepens to reddish brown then gradually decolorised	decolorised	decolorised	decolorised	decolorised	colour slightly fades to yellow
	Re-oxidised with sodium persulphate.	no change	no change	no change	no change	colour partially returns	no change

(12)	Boiled with ferrous sulphate and ammonia for one minute: Filtered Filtrate.	deep red	yellow	orange	brownish	practically decolorised	yellowish
	Filtrate acidified.	yellow	rose pink to deep red	orange	brownish red	faint yellow	do.
(13)	Soln. treated with lead acetate.	no change	yellow to yellow orange when warmed with acetic	no change	no change	no change	reddish yellow ppt.
(14)	,, ,, ,, zinc acetate.	do.	do.	do.	do.	do.	yellow ppt.
(15)	,, ,, ,, barium chloride.	do.	no change	do.	do.	do.	reddish ppt.
(16)	Two or three drops alk. soln. dissolved in 1 ml. conc. H_2SO_4, cooled; few crystals $NaNO_2$ added and warmed in water bath at 80° to 90° C. for 1 min., then cooled in air 2 to 3 mins.	yellow	yellow	violet	yellow	brownish yellow	no change
(17)	Alk. soln. mixed with equal vol. conc. H_2SO_4, a little solid $KMnO_4$ added and boiled for 1 min. Few crystals of resorcinol added and boiled till water evaporated and fuming starts. Poured into soda soln.			strong green fluorescence	——	——	-
(18)	To one vol. alk. soln. add 1 vol. alcohol, 1 vol. ether and one vol. 30% soda and shake: Upper layer.	yellow	yellow	yellow	yellow	colourless	yellow
	Lower layer.	colourless	colourless	colourless	colourless	pink	colourless
(19)	To one vol. alk. soln. add 2 vols. 30% soda, mix and stand 1 min. Add 1 vol. alcohol, 1 vol. ether and shake: Upper layer.	colourless	yellow	yellow	colourless	colourless	yellow
	Lower layer.	yellow	colourless	colourless	red to pink	pink	colourless
(20)	Make acid and extract with petroleum spirit. Petroleum spirit layer.	colourless	colourless	colourless	colourless (ppt. not soluble)	colourless	yellow (faintly yellow suspension)
(21)	Add few drops alcoholic $FeCl_3$ soln. to petroleum spirit layer (No. 20), shake and allow to stand.	no change	no change	no change	no change	no change	greenish brown to greenish black
(22)	To one ml. soln. add dil. acid till just acid, then dil. soda till just alkaline. Add 5 mls. alcohol and 2 drops saturated bromine water. Then add $N/10$ soda, drop by drop.	no change	no change	no change	no change	colour becomes yellow, and on adding $N/10$ soda turns green, then blue, then violet red	colourless, then yellow when alkaline

from alkaline solutions, and wool boiled in the acid solution showed no appreciable colour when spotted with alkali. The boiling of the acid solution resulted, in some cases, in the complete loss of the colouring matter through volatilisation with the steam.

From a consideration of the chemical nature of the prohibited coal tar colours, it was apparent that acidification should give in each case a substance of highly acidic character, which would probably be soluble in an immiscible solvent. This was found to be the case, and methylated ether proved to be an excellent solvent, provided the solution was not too strongly acid. With an acidity greater than that stated in the table, some, or all, of the colour may not be removed by the ether. It is not advisable to wash the ethereal extract with water, as picric acid is partially washed out. From the ethereal solution all except one of the dyes can be re-extracted with dilute alkali. The exception is aurantia, which remains in solution in the methylated ether. If, however, an equal volume of petroleum spirit is added to the methylated ether solution, dilute alkali will now extract aurantia. The colouring matter of gamboge is also of an acidic nature and can be extracted from an acid solution by means of ether, and alkali will remove it from the latter solution.

Practically all animal and vegetable colouring matters naturally present in foodstuffs give no colour to the alkaline solution when treated in the above manner. In addition, most dyes likely to be used to colour foodstuffs are insoluble in ether. Among dyes which might be extracted are simple nitroso dyes, certain acidic non-sulphonated azo dyes, oxazones, simple anthraquinones and phthaleins; but these are rarely used in foodstuffs. The extraction method is therefore of advantage in showing the absence of prohibited dyes very quickly.

Numerous tests were carried out on dilute alkaline solutions of the various colours at concentrations such as might be obtained in practice. The most useful of these tests are given later, and from them a scheme was drawn up for routine work. The scheme enables each dye to be detected, and some of the other tests can be used as confirmation. Tests 18 and 19 used in the general scheme are a little unusual. Test 18 depends upon the salting-out effect of strong soda upon the sodium salt of the dye. Test 19 depends upon a similar effect after a preliminary treatment for 1 minute with strong soda, whereby the dyes with three or more nitro-groups are partly decomposed and behave differently.

SCHEME FOR THE DETECTION OF PROHIBITED COLOURS.

Make an ammoniacal extract of the foodstuffs by any suitable means, filtering, if necessary, and using as large a quantity of material as convenient. To the ammoniacal extract add 1 drop of methyl orange, neutralise with acid, then make acid to the extent of about $N/100$ to $N/50$. Extract once or twice with methylated ether, transferring the ether to a separating funnel. Extract the ether with successive quantities of about 5 to 10 ml. of approximately $N/100$ sodium

hydroxide solution until no more colour is removed. Add an equal quantity of petroleum spirit to the methylated ether and again extract with dilute sodium hydroxide solution.

Absence of colour in alkaline layers indicates absence of prohibited dyes.

<table>
<tr><td rowspan="11">Extract from petroleum spirit and methylated ether is orange-red if aurantia is present. Apply tests 10 and 19.</td><td colspan="3">Extract from methylated ether is coloured yellow by picric acid; yellow to orange by Victoria yellow, Manchester yellow and gamboge; red by aurine.</td></tr>
<tr><td colspan="3">(A). To 1 ml. of solution add 1 ml. alcohol, 1 ml. meth. ether and 1 ml. 30 per cent. sodium hydroxide solution in that order, and shake.</td></tr>
<tr><td>Ethereal solution is colourless and soda solution is pink if aurine is present. Confirm by tests 11 and 22.</td><td colspan="2">Ethereal solution is yellow and soda solution colourless if others are present.</td></tr>
<tr><td colspan="3">(B). To 1 ml. of solution add 2 ml. of 30 per cent. sodium hydroxide solution, mix and leave for 1 minute. Add 1 ml. methylated ether and 1 ml. alcohol and shake.</td></tr>
<tr><td>Ethereal solution is colourless and soda solution is (a) yellow if picric acid is present, (b) pink if aurin is present. A yellow colour in the soda layer may not be seen if both are present. In that event apply the confirmatory tests for picric acid, viz. tests 3, 9, 11, and the formation of picrates with naphthalene, quinine, etc.</td><td colspan="2">Ethereal solution is yellow and soda solution colourless if others are present.</td></tr>
<tr><td colspan="3">(C). To original solution add acid and extract with petroleum spirit.</td></tr>
<tr><td>Ether coloured yellow indicates gamboge. Confirm by tests 21 and 13, 14, 15 (if necessary concentrating the solution).</td><td colspan="2">Victoria yellow and Manchester yellow give colourless petroleum spirit, but on removing this and adding petroleum spirit which has been shaken with ammonia a yellow turbidity is obtained. (Gamboge also gives this.)</td></tr>
<tr><td></td><td>Victoria yellow. Apply test 12.</td><td>Manchester yellow. Apply tests 16 and 17.</td></tr>
</table>

The scheme is put forward as a preliminary attempt to detect the prohibited dyes. It is possible that in certain cases it may fail. It has, however, been in use in this laboratory for nine months, and no interfering colours have yet been extracted.

The author desires to thank the Government Chemist for permission to publish this work.

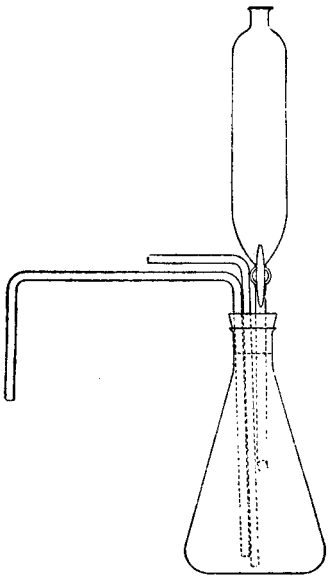
GOVERNMENT LABORATORY, LONDON.

Note.

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.

AN IMPROVED METHOD FOR THE VOLUMETRIC DETERMINATION OF TIN.*

MANY processes have been published for the volumetric determination of tin, based on its reduction to the stannous condition by various metals, and its subsequent determination by titration with a suitable oxidising agent, generally iodine. Whilst some of these give accurate results in the hands of skilled workers who are used to them, the great majority do not admit of using the theoretical factor for calculating tin from the amount of iodine used, but rely on special factors found by reducing and titrating known amounts of tin under the same conditions. Inasmuch as this is evidence of an inherent error, albeit constant and controlable, it constitutes a serious objection to the processes concerned. I have tried iron, nickel and antimony as reducing agents, but have abandoned them for one reason or another. Zinc, according to Sanved (ANALYST, 1927, 2) and the author's, he cites, requires very cautious use, and, in any case, necessitates redissolving the deposited tin. Lead was proposed, as a reducing agent, by Barrett and Sullivan, U.S. Bureau of Mines (*Chem. Age*, June 16, 1923), and has been found satisfactory; no process, however, is on a sound theoretical basis which does not ensure entire exclusion of air throughout the operations, owing to the rapidity of oxidation of stannous chloride; on the other hand, the lead must be withdrawn before titration, and to do this without introduction of air, requires a heavy waste of carbon dioxide and considerable manipulative ability on the part of the analyst.



The process described below has been found accurate and fairly rapid, and the theoretical titration value of the iodine is used, showing that reduction is complete.

The reduction is carried out in the apparatus shown in the figure. The doubly-bent tube must be capable of being slid up or down in the stopper, and when pushed down it must reach to the very bottom of the flask. The tube with the single bend delivers carbon dioxide from a Kipp's apparatus. The solution of tin in about 250 c.c. of dilute hydrochloric acid (50 c.c. of HCl with 200 c.c. of water acts very well) is placed in the flask, a strip of sheet lead, about 20×2 cm., bent into a coil, is dropped in, and the stopper is inserted; *previous to insertion of the stopper the outlet tube with the double bend must be drawn up till its lower end is almost level with the end of the stopper*; the tap of the funnel is closed. The apparatus is placed on the hot plate and a steady stream of carbon dioxide is passed through it; the

* Communication from the Research Department, Woolwich.

solution is boiled for one hour. At the end of this time the outlet tube is closed with a rubber cap, and the flask removed from the plate and allowed to cool under pressure of the Kipp's apparatus. In a flask (capacity 750 c.c.) are placed 20 grms. of sodium oxalate and a measured excess of 0·1 *N* iodine solution. When the tin solution is quite cold the outlet tube is pushed down through the stopper till its end almost touches the bottom of the flask; the flask containing the iodine is placed under the free end of the tube, the rubber cap removed, and the liquid allowed to blow over into the iodine flask under the pressure of the carbon dioxide. With a large Kipp's apparatus this takes place automatically; with a smaller one the same end may be reached by blowing into a tube passing through a cork in the top of the Kipp's apparatus.

As much as possible of the tin solution having been blown over, the outlet tube is pulled up somewhat and the carbon dioxide turned off; 50 c.c. of water are run in through the tapped funnel, care being taken not to let the surface below the tap, the outlet tube is again lowered, the flask and the lead rinsed by shaking, and the wash water driven over, as before, by turning on the carbon dioxide; this washing operation is repeated once. During the blowing-over operations it is desirable to rotate both flasks; the reduction flask, to get as much of the crystallised lead chloride over as possible, the iodine flask, to ensure the tin being oxidised by the iodine with a minimum of delay. The unreduced iodine remaining in the flask is back-titrated with sodium thiosulphate, starch solution being added just before the end; it is advisable to shake well between additions of thiosulphate towards the end of the titration and to allow the flask to stand a few minutes after completion, to make sure that no recurrence of the blue colour takes place, as there appears to be a slight tendency for iodine to be adsorbed on the sodium oxalate and only to react somewhat slowly.

One c.c. of 0·1 *N* iodine solution reduced by the stannous chloride = 0·005935 grms. of tin (the theoretical amount).

The following results were obtained in tests carried out:

Tin taken. Grm.	Titration with $Na_2S_2O_3$ solution. C.c.	Tin corresponding to *1·0 c.c. of $Na_2S_2O_3$ solution. Grm.	Tin found. Grm.
0·2000	28·55 − 8·75 = 19·80	0·01014	0·2008
0·1700	28·55 − 11·70 = 16·85	0·01014	0·1708
0·1400	29·20 − 15·35 = 13·85	0·01014	0·1404
†0·1100	29·20 − 18·20 = 11·00	0·01014	0·1115
0·0800	28·55 − 20·70 = 7·85	0·01014	0·0796
0·0400	29·20 − 25·30 = 3·90	0·01014	0·0395

Experiments showed that 20 grms. of sodium oxalate had no influence on the titration of iodine by thiosulphate so long as hydrochloric acid was also added; in the absence of the acid it caused low results, due, possibly, to alkalinity of the oxalate.

B. S. EVANS.

* This figure was calculated from the standardisation of the thiosulphate solution against a weighed amount of iodine.

† This titration was not very satisfactory, as the colour kept recurring.

Notes from the Reports of Public Analysts.

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

CITY OF LEICESTER.

Report of the City Analyst for the Year 1926.

Of the 650 samples examined during the year, 265 were purchased informally. More than half (382) of the samples were milks.

Bacteriological Examination of Milk.—The total number of bottled milks of all grades bacteriologically examined was 208, of which 157 were passed as complying with the standards (Analyst, 1923, **48**, 120), whilst in 23 the total count was too high, and in 46 *B. coli* were too numerous.

Alcohol in British Wines.—Thirteen samples were examined. A "non-alcoholic" orange wine contained only 0·4 per cent. of alcohol, whilst a "raisin wine" contained 11·2 per cent. (by weight). A "non-alcoholic" ginger wine contained 0·65 per cent., a "ginger wine" 9·7 per cent., and a cowslip wine 13 per cent. of alcohol by weight. As the public probably do not distinguish between wines having apparently similar names, but varying greatly in the amount of alcohol they contain, it would be an advantage if the alcoholic strength were stated on the label.

S. F. Burford.

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.

THE MEANING OF THE TERM "DRIPPING."

On July 5th, in the Dublin Circuit Court, Judge Davitt gave his reserved judgment in four appeals, by tradesmen in County Dublin, from a decision of the District Justice, who had fined them for selling dripping not of the nature, substance and quality demanded, since it had been proved to be rendered beef or mutton fat not containing any of the extractive matter which falls from roasting meat.

At the hearing of the appeal, Mr. Geoghegan, K.C., appearing for the Dublin County Council, contended that if a purchaser got a substance which lacked certain ingredients and characteristics, such as aroma, smell and flavour, he got a different article from that demanded, and, accordingly, however excellent the different article might be, an offence had been committed.

The certificate of the Public Analyst (Mr. B. G. Fagan) stated: "I am of opinion that the said sample was not genuine dripping. It proved to be rendered beef or mutton fat. This opinion is based on the fact that dripping should be the fat that falls from roasting meat, and, as such, contains certain extractive matter from the meat, whereas the said sample did not contain any such extractive matter, and had not the appearance usually associated with dripping."

Mr. Geoghegan read the certificate of Dr. Hugh Ryan, State Analyst, which was as follows: "I am of opinion that the sample in question consists of fat obtained by rendering beef or mutton, or a mixture of these fats. There appears to be no Statute, Act or Order defining 'dripping' at present in force in *Saorstat Eireann*. The term must, therefore, be deemed to have whatever meaning is given to it in common parlance. The fat got from beef or mutton by roasting, and also that obtained from these substances by 'rendering' with hot water or steam, are known as 'dripping'."

Mr. Fagan admitted that there was practically no difference between the chemical constituents of genuine dripping and the sample; both consisted almost entirely of fat.

Evidence was given by a representative of the manufacturers that the article in question was a fine edible fat. It had been made for 50 or 60 years in their Liverpool factory, and for 30 or 40 years in their Dublin factory. It had always been sold as dripping.

Miss P. Ryan, Public Analyst, Dublin, gave evidence that the sample, which she had analysed, would have a better preservative action than ordinary dripping, and Mr. J. B. McKean, F.I.C., stated that, in his opinion, the article could properly be described as dripping.

In his judgment the Judge said that, whatever the original meaning of the word "dripping" might have been, this substance had been sold in shops for forty or fifty years as dripping. After such a long period he could not hold that what was always sold as dripping was not dripping now. He, therefore, reversed the decision of the District Justice.

Federated Malay States.

ANNUAL REPORT OF THE CHEMIST, INSTITUTE FOR MEDICAL RESEARCH, FOR 1926.

THE chemical work of the Medical, Trade and Customs, Police, Railway, Public Works, and Forest Departments, is carried out, wholly or in part, in the Chemical Laboratory of the Institute for Medical Research, Kuala Lumpur, under the direction of Mr. R. W. Blair, F.I.C.

The total number of samples examined in 1926 was 7756, as compared with 6021 in 1925 (*cf.* ANALYST, 1927, 158).

MILK.—Of the 600 samples examined, 53 contained less than the statutory 3·25 per cent. of fat, and 63 less than 8·5 per cent. of solids-not-fat. The reductase test, applied in a similar way to the New Zealand test (*cf.* ANALYST, 1927, 234), was made on 64 samples, of which 47 completely decolorised the methylene blue in 3 hours.

WATER.—The jungle streams of the Federated Malay States are the chief sources of supply, and are, as a rule, free from pollution. Chemical examinations were made of 528 samples and bacteriological examinations of 99. The chlorination of the Klang water supply has been continued, the average amount of chlorine added being 1 part in 1·35 millions.

SEWAGE EFFLUENTS.—Various types of sewage installations have been erected in Selangor. In the majority of cases the effluents did not conform to the standards prescribed in the Report of the Royal Commission on Sewage Disposal.

TODDY.—During the year there were examined 171 samples to ascertain whether they complied with the standards of the Sale of Food and Drugs Enactment, 1913, *viz.* that toddy must not contain more than 10 per cent. of alcohol by volume, or have an acidity exceeding 0·8 per cent. expressed in terms of acetic acid. Eight of the samples showed acidity in excess of this amount. It is probable that most of the toddy offered for sale is diluted with water, but no satisfactory method of detecting this adulteration has yet been devised.

TOXICOLOGICAL ANALYSES.—Thirteen exhibits examined for the Medical Department included viscera, foods and medicines. In one case a small quantity of an alkaloid giving reactions characteristic of nicotine was extracted, and in a case of opium poisoning the stomach washings were found to contain opium.

One of five medicines examined contained "ganja" (*Cannabis indica*). A red powder resembling mercuric iodide in appearance was found to consist of precipitated barium sulphate with a red dye adsorbed, and a small quantity of mercuric iodide.

Department of Scientific and Industrial Research.

FUEL RESEARCH. PHYSICAL AND CHEMICAL SURVEY OF THE NATIONAL COAL RESOURCES, No. 7.

METHODS OF COAL ANALYSIS.*

THE Report follows the publication of an interim Report in 1923 (ANALYST, 1924, **49**, 36), followed by a Report on the determination of nitrogen in coal (ANALYST, 1924, **49**, 230), and gives a number of changes in the methods proposed (mostly of a minor character), which have resulted from further practical experience. Periodical review of the publication is proposed, so as to provide an authoritative statement of the best current practice in the methods of valuing coal.

PROXIMATE ANALYSIS.—*Determination of Moisture.*—One to two grms. of finely powdered coal (air dried and passing a 60-mesh I.M.M. sieve) are weighed into a shallow vessel with a cover, and the uncovered coal heated for 1 hour at 105–110° C., covered, cooled in a desiccator over sulphuric acid, and weighed. There should not be more than 0·3 grm. of coal per sq. cm. of dish, and where the coal is specially liable to oxidation a current of dry nitrogen or carbon dioxide should be used.

Ash.—One to two grms. of the finely ground coal are heated in a dish, about 1 cm. deep by 5 cm. in diameter, first slowly, then to 750°–800° C., in an oxidising atmosphere to constant weight.

Volatile Matter (less moisture).—One grm. of the powdered coal is heated, preferably in a gas or electrically heated muffle or tube furnace, for 7 minutes, at a temperature of 925° C. +25° in a platinum crucible, closed by a well-fitting internal capsule lid, and supported on a platinum or nichrome wire. The percentage of moisture is deducted from the value found.

"Fixed Carbon."—This value is obtained by subtracting the sum of the percentages of moisture, ash and volatile matter from 100, and the words should appear in inverted commas.

* Obtainable at Adastral House, Kingsway, W.C.2. Price 9d. net.

ULTIMATE ANALYSIS.—*Determination of Carbon and Hydrogen.*—A purifying train in duplicate for air and oxygen is connected with the combustion tube, which is supported on a furnace capable of giving a temperature of at least 800° C., and the absorption train collects the moisture and carbon dioxide (J. G. King and D. MacDougall, *Fuel in Science and Practice*, 1926, **5**, 33). It may be necessary to determine carbonates by one of the following methods:—Dittmar (*Quantitative Chemical Analysis*); Lunge and Rittener (*Technical Methods of Chemical Analysis*), or some modification, such as that of F. S. Sinnatt and W. Harrison (*The Determination of Carbon Dioxide in Coal*), or the method of the Lancashire and Cheshire Coal Research Association, Bulletin No. 7, 1920 (See Appendix I.). An approximate correction for water of constitution may be applied if the quantitative composition of the ash is known.

Determination of Sulphur.—This is recommended to be made by the Eschka method of ignition with light calcined magnesia and anhydrous sodium carbonate. If more than 2 per cent. of sulphur is present, only 0·5 grm. of sample should be taken for the determination, and the figure should be checked by a calorimetric bomb combustion. The amount of sulphur in the ash should be deducted from total sulphur, and the difference reported as "combustible sulphur." It is determined as in Technical Paper 254, U.S.A. Bureau of Mines, 1921 (A. R. Powell, *The Analysis of Sulphur Forms in Coal*).

Nitrogen is determined by the Kjeldahl method, 1 grm. of coal ground to pass a 100 mesh I.M.M. sieve being used.

Oxygen.—This is usually obtained by difference, and, in view of the inaccuracy of the figure, should be returned in commercial analyses as "Difference (oxygen and errors)."

CAKING INDEX OF COAL.—This is determined by a modification of the Campredon test, and in the case of Scotch coals the results obtained show a close agreement between the caking index and the practical determination of the value of the coke produced by heating the ground coal in cotton bags in the coke oven (*cf.* Thomas Gray, "The Determination of the Caking Power of Coal," *Fuel in Science and Practice*, 1923, **2**, 42).

THE CALORIFIC VALUE OF COAL.—The method to be used for obtaining the calorific value of coal is described in detail, together with the necessary corrections (*cf.* G. N. Huntly, "The Accuracy obtainable in Fuel Calorimetry," *J. Soc. Chem. Ind.*, 1910, **29**, 217, and "Corrections in Bomb Calorimetry," ANALYST, 1915, **40**, 41).

LABORATORY CARBONISATION ASSAY OF COAL.—The Grey and King Method is recommended for this assay (*Fuel Research Board Tech. Paper*, No. 1), or for quick determination of the carbonising characters, the Lessing method.

APPENDIX I., by F. S. Sinnatt and W. Harrison, deals with the Determination of the Carbon Dioxide in Coal, and is abstracted from the Lancashire and Cheshire Coal Research Assoc. Bull., No. 7, 1920.

APPENDIX No. II. is concerned with Abnormalities in Phosphorus Determinations. *Arsenic.*—If arsenic is present in the coal the temperature of the test solution should be kept below 45° C., and it is advantageous to remove the arsenic (Fresenius, *Anleit. z. quant. chem. Anal.*, Braunschweig, 1875, **1**, 421; Campbell, *J. Anal. Chem.*, 1888, **2**, 370; *J. Anal. App. Chem.*, 1893, **7**, 2; Maderna, *Atti R. Accad. Lincei*, 1910, **19**, ii, 15). Silicomolybdate is a serious impurity (Jörgenson, ANALYST, 1926, **51**, 67) in the phosphomolybdate precipitate, and titanium behaves as a retardent or inhibitant (Mellor, *A Treatise on Quantitative Inorganic Analysis*,

Griffin, 1913). Vanadium also has a retarding action and is precipitated with phosphorus. Before passing a residue as free from phosphorus it should be fused with sodium carbonate, leached and precipitated as usual, whilst filtrates should be tested by adding more molybdate and allowing them to stand.

D. G. H.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Ammonia Content of Cold-Storage Eggs. H. C. Lythzoe. (*Ind. Eng. Chem.*, 1927, **19**, 922–924.) The Massachusetts cold-storage egg law provides that such eggs shall be sold from a container plainly marked, "Cold-Storage Eggs." The time is not mentioned in this law, but similar legislation in other States requires a 30-day period to elapse before the eggs are considered to be cold-storage eggs. The determination of the ammonia content has been successfully used for many years by the Massachusetts Department of Public Health as a means of differentiating between fresh and old edible eggs. In the present experiments the ammonia content of 1088 cold-storage eggs, representative of retail sales during the past five years, was determined by means of Folin's aeration method, with Nessler's solution as the reagent. Two hours' aeration was sufficient to recover all the ammonia. The figures, segregated by months, were compiled as a summation series, and plotted upon logarithmic-probability scales (Whipple, *J. Franklin Inst.*, 1916, **182**, 37, 205). Assuming that the difference in ammonia content between cold-storage eggs sold in September and in October would be relatively the same as between those sold in October and November, and those sold in November and December, the estimated September lines were drawn on the chart, and the following values (mgrms. of ammonia per 100 grms.) were obtained :—

Average ammonia content on the fifteenth of months :

	Lower Quartile.	Median.	Upper Quartile.
September	2·1	2·4	2·8
October	2·3	2·6	2·9
November	2·5	2·9	3·1
December	2·6	2·9	3·2
January	2·7	2·9	3·2
February	2·8	3·2	3·5

It is to be expected that 25 per cent. of commercial cold-storage eggs will be above the upper quartile, and 25 per cent. will be below the lower quartile, in ammonia

content.* The results of the analyses are plotted upon logarithmic-probability scales, and the points form a straight line between 2·1 and 4·3 mgrms. of ammonia, and represent about 95 per cent. of the total samples. It may therefore be assumed that it is improbable, but not impossible, for commercial cold-storage eggs to contain less than 2·1 mgrms. of ammonia per 100 grms. Although some of the eggs contained over 4 mgrms. (per 100 grms.) of ammonia, and were not perceptibly rotten, as judged by the odour, this fact cannot be construed as showing that such eggs were not decomposed, because a considerable proportion of the excess of ammonia in such " shell eggs " is caused by evaporation, which increases the fat as well as the ammonia.

Action of Ethylene on Pure Starch. H. E. Rea and R. D. Mullinix. (*J. Amer. Chem. Soc.*, 1927, **49**, 2116–2117.)—It has been found by Harvey and Regeimbal (" Physiology of Blanching Celery," *Proc. Amer. Assoc. Advancement Sci.*, 1924, **79**) that fruits and vegetables treated with ethylene have a higher sugar content than the same kind of fruits and vegetables not treated with the gas. An attempt was made to change pure starch into sugar by the use of ethylene, since ripening is accompanied by change of starch into sugar. *Dry* starch in an atmosphere of ethylene at 21°C. and at atmospheric pressure was partly changed into a reducing sugar, but less rapidly than starch emulsion with water. Three starch emulsions (1 grm. of starch in 100 c.c. of water) of different " boiling times " were saturated with ethylene at 22°C. and allowed to stand. The first had been boiled one minute, the second five, and the third ten minutes, and all were cooled to room temperature and then saturated with the gas. The rate of conversion of the starch into sugar was affected by the time of boiling ; the mixture boiled for 10 minutes was changed more rapidly than that boiled for one minute. A table and graphs show the results. After 168 hours a 10 c.c. sample of the first emulsion reduced 4 c.c. of Fehling solution, one of the second reduced 7 c.c., and one of the third reduced 6 c.c. The second then showed 57 per cent. of reducing sugar. Plateaux in the curve for the mixture boiled for ten minutes have not yet been explained. It appears that an enzyme need not be present for the conversion of starch into sugar by the action of ethylene. The presence of ethylene alone

* If a number of observations are arranged in order of size or quality, etc., the mid value of the variable is the *median*, and those values half way between the median and the ends of the series are the *quartiles*. Twenty-five per cent. of the observations lie below the lower quartile, 50 per cent. below the median, and 75 per cent. below the upper quartile.

A *Frequency Distribution* shows the number of times an event happens in a particular way, and the formula used to describe such a distribution is a *Frequency Curve*. If the frequency curve representing the distribution of the observations is plotted, then the area enclosed between any two ordinates is proportional to the number of observations falling between the corresponding values of the variable. The value of the variable at which the ordinate divides the area of the curve into two equal parts is the median. The upper and lower quartiles are those values of the variable at which the ordinates cut off one quarter of the area of the curve at its two extremities. The two quartiles, together with the median, divide the total frequency into four classes of equal frequency.

A diagram illustrating the graphing of quartiles is given, facing p. 106 of Bowley's *Elements of Statistics* (P. S. King & Son, 1920 Edition). The terms were introduced by Sir Francis Galton, but are not much used now.—EDITOR.

seems sufficient. The chemistry of the reactions is not known, but it is thought that the gas acts as a catalytic agent, since no absorption was noticed, even upon long standing. The work will be continued at high temperatures and pressures.

P. H. P.

Analysis of "Fruit and Apple" Jams. C. F. Muttelet. (*Ann. Falsif.*, 1927, **20**, 391–394.) For the correct description of jams and jellies under French law it is necessary to know the relative quantities of apple and "other fruit" present, and particularly which of the two predominates. To arrive at this figure malic and citric acids should be determined (ANALYST, 1922, **47**, 398.) Jams and jellies contain about 64 per cent. of added sucrose and invert sugar, so that about 36 per cent. of fruit substance is present. If this consists of 18 per cent. apple and 18 per cent. "fruits," the quantities of citric acid corresponding to this percentage of fruit would be: Black currant and apple jelly, 0·54; gooseberry and apple jelly, 0·36; raspberry and apple jelly, 0·27; and strawberry and apple jam, 0·18; and these figures are minima for the application of the description "fruit et pommes." For lower percentages the description would have to be "gelée ou comfiture de pommes aux—." Thus a strawberry and apple jam having 0·05 per cent. of malic acid and 0·19 per cent. of citric acid may be regarded as containing 18 per cent. of strawberry, but an "apple and gooseberry jelly" showing 0·09 and 0·17 per cent., respectively, would only contain a maximum of 10 per cent. of gooseberry, and is incorrectly described. At times citric acid may be added to raise the acidity, and then the figures may show an absence of apple, which raises suspicion.

D. G. H.

Bulgarian Honey and Beeswax. J. Zoneff. (*Z. Unters. Lebensm.*, 1927, **53**, 353–376.)—A statistical survey is made of honey and wax production in Bulgaria, and complete analyses of 190 samples of the former and 136 of the latter have been made as an aid to their evaluation. The methods employed are described, and the mean of the values obtained are as follows:—*Honey.* Sp. gr. of a solution (1+2) at 15°C., 1·116; water content, 21·28 per cent.; polarisation readings of 10 per cent. solutions in a 200 mm. tube at 20°C., 2·28° and 2·63°, before and after inversion, respectively. The sucrose content was usually less than 3 per cent.; invert sugar, 71·74 and 73·23 per cent. before and after inversion, respectively. The non-sugars and acidities were within the normal limits for natural honeys, but the ash was usually higher than 0·1 per cent. Nitrogen was 0·935 per cent. Catalase was detected in all the samples. The relative merits of the tannin and phosphotungstic acid methods for the determination of protein substances are discussed, and a number of qualitative tests described. The microscopical examination took the form of the study of the nature and quantity of the pollen present. *Wax.*—The following are the extreme values of the average constants obtained for 136 waxes from 12 localities. Sp. gr. (15° C.), 0·963 to 0·965; refractometer reading, (40° C.) 43·70 to 46·00; m. pt., 63° to 64° C.; solidif. pt., 62° C., acid value, 18·4 to 20·8; saponification value, 90·8 to 95·7; ester value, 72·0 to 74·9; iodine value, 8·3 to 11·4; Buchner value 1·6 to 2·8.

The Buchner value is the number of c.c. of a 0·1 *N* solution of alcoholic potassium hydroxide required to neutralise 2·5 grms. of wax dissolved in alcohol (80 per cent.).

J. G.

Analysis of Honey. F. Lucius. (*Z. Unters. Lebensm.*, 1927, **53**, 376–381.)—Sources of error in the author's method for the determination of sugars in honey (ANALYST, 1926, **51**, 581) are indicated. In the removal of dextrinous matter, results almost 2 per cent. higher are obtained if the extraction is carried out at 0° C. instead of at 20° C. It is recommended that 100 c.c. of ether at 20° C., or 70 c.c. at 0° C. be used. The subsequent polarimetric determination is not affected. A curve has also been plotted showing the effect of mixtures in various proportions of ether and alcohol on the solubility of glucose. Since the solubility is increased by the presence of fructose, this must be taken into account in the determination of the volume of ether to be used for honeys in which the relative proportions of these sugars are abnormal. J. G.

Method for the Detection of Fruit Wine in Grape Wine. K. Müller, E. Vogt and O. Raesch. (*Z. Unters. Lebensm.*, 1927, **53**, 331–334.)—Experiments have been carried out on a large variety of treated, untreated, pure and adulterated wines in order to test the methods of Reich (*Weinbau and Kellerwirtschaft*, 1926, 220) and of Röttgen (*Deutsche Wein-Ztg.*, 1926, No. 27) for the detection of fruit wine in grape wine. Neither method is described, but both involve the use of the quartz lamp, and in the latter method the wine is first neutralised and treated with an ammoniacal copper acetate solution. The colour of the light produced depends on the nature and condition of the wine, which should be filtered, as certain cloudy, brown wines give false results. Pure white wine gives a whitish-grey fluorescence by Reich's method, and a blue colour by Röttgen's method. Dark wines, however, give a brown colour similar to that given by fruit wines. Consequently the detection of such wines is not easy other than by comparison with a standard wine of known purity, when 10 to 20 per cent. of fruit wine may be detected. Fruit wine reacts as grape wine if it is treated with "*Éponit*" or casein and then added to the grape wine, or if the mixed musts are fermented together. The Röttgen method is preferred, but is recommended only as a means of indicating the possibility of adulteration. In an added note it is stated that Reich now prefers to use an ethereal extract of the wine absorbed in filter-paper.

J. G.

Detection of Fruit Wine in Grape Wine. M. Rüdiger and W. Diemair. (*Z. Unters. Lebensm.*, 1927, **53**, 335–340.)—The Schaffer modification of the Schaffer–Schuppli method for the detection of fruit wines in grape wine (ANALYST, 1924, 235) is criticised, and amended as follows:—The wine (50 c.c.) is shaken at ordinary temperatures with 1 grm. of the purest animal charcoal for 30 minutes, filtered, and exactly neutralised to azolitmin paper, with a saturated solution of baryta. The precipitate is removed by the centrifuge or by filtration, and 5 c.c. of the filtrate are well mixed with two drops of 0·2 *N* silver nitrate solution and 0·5 c.c. of 0·2 *N* sodium hydroxide solution, and allowed to stand in the

dark. Fruit wines gave a brown or black colour in a few minutes, and, of 26 white grape wines, 19 remained colourless after 30 minutes, 5 gave a yellow colour, whilst 2 had a brown tinge. Of 26 grape wines adulterated with 20 per cent. of fruit wine, 17 gave positive reactions, 4 doubtful reactions, and 4 negative reactions. In one case an adulteration of 60 per cent. gave only a weak reaction. It is concluded that the reaction depends on the nature, amount and state of combination of the tannin in the wine, since, although a 0·05 per cent. solution of tannin itself gave a reaction similar to that of fruit wine, it gave only a weak reaction when mixed with a pure grape wine. The neutralisation procedure and the extraction with charcoal appear to exercise an influence in this respect. It is concluded that the sensitiveness of the reaction depends on the composition of the grape wine and of its adulterant, and that 20 per cent. of the latter is usually detectable, and in certain cases 10 per cent. J. G.

Determination of the Hydrogen Ion Concentration of Wine by means of the Quinhydrone Electrode. R. Dietzel and E. Rosenbaum. (*Z. Unters. Lebensm.*, 1927, **53**, 321–330.)—The acid taste of wines is attributed primarily to the " degree of acidity," or the concentration (in mgrms.) of hydrogen ions per litre of wine. The theory and technique of the simple quinhydrone electrode method for the determination of the P_H value of 10 c.c. of wine are described. The method is recommended, since the colorimetric method cannot be used with coloured liquids, and the hydrogen electrode may be poisoned by any sulphur dioxide in the wine. The results are given for a number of white, red and sparkling wines (1921 to 1925), together with the total acidity of the wine, calculated as tartaric acid. The extreme P_H values recorded are 2·65 and 3·56, corresponding with 9·5 and 6·1 grms. of tartaric acid per litre. In general, sparkling wines have the lowest P_H values, whilst those of the red and white wines are very similar. Tables are given correlating P_H values and " degrees of acidity " for any desired range. J. G.

" Mikrobin " in Wine. C. von der Heide and R. Föllen. (*Z. Unters. Lebensm.*, 1927, **53**, 487–509.)—To determine "mikrobin" (sodium *p*-chlorobenzoate) in wine, it is necessary to separate the acid either by distilling the acidified wine in a current of steam or by extracting it with ether. The solution is evaporated in a platinum dish on a water-bath, small quantities of halogen-free sodium peroxide being added from time to time. After gentle ignition, sufficient only to char the carbonaceous matter present, the dry residue obtained is extracted with water and filtered off, the filtrate and washings being concentrated, if necessary, and then treated with silver nitrate solution and carefully acidified with nitric acid. The silver chloride formed is weighed in the usual way. The addition of mikrobin to foodstuffs or wine is regarded as inadmissible. T. H. P.

Determination of Cineole in Camphor Oil. T. T. Cocking. (*Pharm. J.*, 1927, **118**, 725–727.)—The method used for the determination of cineole in eucalyptus oil may be applied to oils containing less than 50 per cent. of cineole

by adding an equal weight of pure cresineol to the test mixture before determining the freezing point, but the effect of the natural constituents of cineole-containing oils on the freezing point requires to be known when using the eucalyptus oil curve. In the case of camphor oil the effect of the camphor is to raise the freezing point, the maximum increase being for a saturated solution of camphor in cineole, when the error approximates to 3·5 per cent. of cineole. When the diluent contains 25 per cent. of camphor the error is less than 1 per cent., and for light camphor oils boiling below 200° C. the error is negligible. Tables are given indicating the corrections necessary for mixtures of cineole and camphor, and terpene and cineole saturated with camphor. Crude camphor oils containing high boiling constituents should be distilled through a fractionating column until camphor solidifies in the condenser, and the cineole should then be determined in the distillate. Results will be slightly low. (*Cf.* ANALYST, 1920, **45**, 370; 1927, 276.) D. G. H.

Alkaloidal Hydroferrocyanides and their Analytical Uses. M. Gadreau. (*J. Pharm. Chim.*, 1927, **119**, 145–151.)—Hydroferrocyanic acid is not a specific reagent for tertiary amines, but strychnine or brucine may be gravimetrically determined by its means when only one of these bases is present in solution. Strychnine may be separated from brucine by three successive precipitations, in which very dilute solutions of the alkaloids are used. An excess of potassium ferrocyanide and hydrochloric acid is added, the solution filtered after 30 minutes, and the precipitate washed, suspended in chloroform, treated with ammonium hydroxide, and the alkaloids separated, exact details of manipulation being adhered to. The precipitate is redissolved in distilled water with a little hydrochloric acid, and a second precipitation carried out. Less brucine is present in this precipitate, and a third precipitation reduces the quantity still further, the weight of strychnine hydroferrocyanide obtained being within 1 to 2 per cent. of the theoretical yield. The combination of nux vomica alkaloids with chloroform may be destroyed by boiling in distilled water. Commercial brucine may be purified by preparing the easily crystallisable hydroferrocyanide. The hydroferrocyanides of hordenine, emetine, cepheline, eserine and tropine were found to correspond to the general formula of 1 mol. of alkaloid and 1 mol. of hydroferrocyanic acid. D. G. H.

Colour Test for Ergot Alkaloids. N. Evers. (*Pharm. J.*, 1927, **118**, 721–722.)—Two grms. of the powdered ergot are shaken for 2 hours with 1 c.c. of 10 per cent. ammonium hydroxide 2 c.c. of water and 40 c.c. of ether, or 2 c.c. of *Ext. Ergotae Liq.* are mixed with 1 c.c. of 10 per cent. ammonia and shaken with 15, 10 and 5 c.c. of ether. The ethereal extract in either case is filtered, evaporated to dryness, the residue taken up with 15 c.c. of glacial acetic acid, the solution filtered, and 4 c.c. of filtrate mixed with 4 c.c. of 50 per cent. (v/v) sulphuric acid in a test tube. The full colour takes about 12 hours to develop, and all colours are matched in a Lovibond tintometer. All preparations with amounts of alkaloid above 0·065 per cent. by the biological test gave a well-marked colour, and a

negative test was always found to denote physiological inactivity. Ergotoxine phosphate and ergotinine citrate may be similarly tested by suspending them in 20 c.c. of water and extracting the mixture, and as little as 0·05 mgrm. of alkaloid may be detected; amounts greater than 0·7 mgrm., however, give too intense a colour for reading. D. G. H.

Sulphur Sublimation. C. O. Griffiths. (*Pharm. J.*, 1927, **118**, 734–735.)—A critical examination of sublimed sulphur suggested a modification of the B.P. description of the product. Sublimed sulphur may be defined as a slightly gritty, bright yellow powder, almost odourless and tasteless, consisting microscopically of almost opaque globules, mostly in strings, associated with an occasional angular mass. On mixing 10 grms. of the sample with water, filtering and thoroughly washing, the mixed filtrate and washings should require for neutralisation not more than 5 ml. of 0·1 *N* sodium hydroxide solution, and not more than 80 per cent. of soluble matter should be present when 5 grms. of the finely powdered sulphur are shaken with 100 ml. of carbon disulphide at frequent intervals for 30 minutes in a corked flask, 10 ml. of the filtered solution evaporated to dryness, and the residue dried at 80° C. until the loss in weight during 1 hour does not exceed 0·001 grm. The arsenic limit should be 5 parts per million. (*Cf.* ANALYST, 1926, **51**, 239.) D. G. H.

Effect of Polarised Light on the Pharmacological Properties of Some Drugs. D. I. Macht and W. T. Anderson, Jr. (*J. Amer. Chem. Soc.*, 1927, **49**, 2017–2034).—The effect of polarised light of different wave-lengths was studied on a number of drugs, and more particularly on tincture of digitalis, solutions of cocaine and its salts, and quinine. Polarised light was obtained by the two classical methods: (A) with a Nicol prism, and (B) by means of piles of glass plates. Controls were carefully made with non-polarised light of exactly the same physical properties, and with the same physical constants except as to polarisation. Irradiation with polarised light produced a change in the potency of digitalis tincture. With polarised ultra-violet light a further change or decomposition in its constituents was produced; but, in this case, the tincture became actually more poisonous, as indicated by experiments on cats, pigeons and plants. The emetic properties were increased. Since tincture of digitalis is a complex of a large number of active principles, the chemical nature of which is not definitely known, the result is not surprising. In the case of cocaine, irradiations with polarised light of both short and long wave-lengths produced a deterioration of the drug solution. Circularly polarised light produced even greater deterioration of tincture of digitalis than did plane-polarised light. It was found that polarised light produced, beyond any doubt, a very definite change in the pharmacological properties of the drugs studied, as compared with the normal specimens and with specimens irradiated by non-polarised light. Perhaps the most remarkable fact in this connection is that such changes are produced by polarised light of the ordinary or visible spectrum. This is of practical importance, since polarised light is not so uncommon as might be supposed. When light is reflected from

smooth surfaces, or passes through certain transparent media, a little polarisation occurs. Some tincture of digitalis was placed in two similar flint glass bottles. One bottle was wrapped in thin tissue paper, and the two were left for several weeks in the sunlight, and then the contents were assayed by the plant-method and the cat method. Although less than one-sixth of the quantity of light which passed through the uncovered bottle passed through the covered specimen, yet the covered specimen of digitalis had deteriorated very much more. There was a difference of nearly 15 per cent. in the lethal doses. These results are no more striking than the fact that solutions of organic chemicals with an asymmetric carbon atom can turn the plane of polarised light to the right or left. If " for every action there is a reaction," then possibly if a solution affects polarised light, *vice versa* polarised light may react on the solution and produce some rearrangement of its molecules. P. H. P.

Biochemical, etc.

Quantitative Determination of Iron in Tissues. R. P. Kennedy. (*J. Biol. Chem.*, 1927, **74**, 385–391.)—A method for the quantitative determination of iron in tissue is described. The iron contained in the animal organism is too small in amount for the usual volumetric or gravimetric methods. The procedure suggested is a simplification of the colorimetric methods hitherto proposed, and attains an accuracy limited only by the optical measurement of colour. It involves the digestion of organic matter in a mixture of perchloric and sulphuric acids and dilution to a known volume. An aliquot portion is treated with a concentrated solution of sodium thiocyanate, and the resulting ferric salt is extracted with amyl alcohol. The alcoholic solution is compared in a colorimeter with a similar solution developed from a known amount of iron. This method has been applied to haemoglobin analysis of blood solutions, and the analyses obtained compare favourably with those made by the oxygen capacity and spectrophotometric methods. Some data are given in table form on the iron content of dog tissues, and a discussion on the present work and that of previous investigators on the same subject follows. P. H. P.

Determination of Lactic Acid in Blood. E. Ronzoni and Z. Wallen-Lawrence. (*J. Biol. Chem.*, 1927, **74**, 363-377.)—Lactic acid may be determined in pure solution in quantities of the order of 0·2 mgrm. by the permanganate or sulphuric acid methods, if the aldehyde titration is used, with an accuracy of 98 $\pm$ 3 per cent. The lactic acid of blood determined on tungstic acid filtrates is about 10 mgrms. per cent. higher by the sulphuric acid method. The permanganate method probably more nearly represents the true lactic acid content of the blood, as the yield of carbon monoxide by the sulphuric acid method (assuming that its source is lactic acid) corresponds with the aldehyde by the permanganate method. Considerable retention of lactic acid may occur with precipitation of the proteins ; the more concentrated the protein solution the greater the retention. When mercuric nitrate precipitation is used, the P_H at which

the mercuric oxide is precipitated has a marked effect on the completeness of protein precipitation and on the retention of lactic acid. A P_H value of 7·0 is the optimum point between failure of precipitation of protein on the acid side and greater loss of lactic acid on the alkaline side. Details of the precipitation procedure by mercuric nitrate for hydrolysed blood are given. The acid present is neutralised with sodium hydroxide, and spotting with blue litmus paper is the easiest way to determine the desired alkalinity. At the correct P_H value the precipitate will be granular, and filtration will be rapid and leave a clear, colourless filtrate. If too alkaline, filtration is slow and the filtrate cloudy. If too acid, a drop of sodium hydroxide may be added and the solution refiltered. The hydrogen sulphide is removed by aeration followed by the addition of one drop of copper sulphate. From this filtrate 94 per cent. of the lactic acid known to be present can be recovered as aldehyde. The lactic acid remains constant in filtrates for as long as 72 hours at refrigerator temperature, but occasional changes have been noted in tungstic acid and metaphosphoric acid filtrates left at room temperature.

P. H. P.

Cod Liver Oil as Food. Observations on the Existence of Vitamin *E*. V. E. Nelson, R. L. Jones, G. Adams and L. T. Anderegg. (*Ind. Eng. Chem.*, 1927, **19**, 840–844.)—Feeding experiments on rats showed that a synthetic ration of casein, salts, yeast, dextrin, and cod liver oil as the sole source of fat-soluble vitamins was sufficient for normal growth and normal reproduction. The results, as regards reproduction, were better than those obtained when filtered butter fat was used, but depended on the manner in which the oil was administered, and were best when the oil was mixed with the ration daily. W. P. S.

Bacteriological.

Cultivation of Streptococci. H. Haxthausen. (*Lancet*, 1927, **112**, 370.)—Streptococci from the skin can be cultivated in the presence of staphylococci by taking advantage of the fact that crystal violet in weak concentration inhibits the growth of the latter, but not of the former. A suitable solid culture medium consists of 10 per cent. blood-agar, to which crystal violet (1 : 100,000) has been added. The addition of blood promotes the growth of the streptococci, and enables the small, rather inconspicuous colonies to be readily recognised, since they are nearly always surrounded by a distinct haemolytic zone.

Use of Certain Carbohydrates and Glucosides in the Differentiation of Members of the Salmonella Group of Bacilli. F. Wokes and J. H. Irwin. (*Pharm. J.*, 1927, **118**, 747–751.)—Twenty-one members of the *Salmonella* group of bacilli were examined by a series of serological animal tests. Immune sera were prepared and used to inject into rabbits, and after 10 doses the healthy animals were killed and the high titre sera were separated. The titre of each serum was determined against its specific organism and then against all the other organisms. Assuming nearness in agglutination titre to correspond

with closeness in relationship, a quantitative classification was thus obtained. Results were compared with those from biochemical tests on a series of 24 alcohols, carbohydrates and glucosides, of which arabinose, xylose, sorbitol, mannitol, dulcitol, mannose, sucrose and maltose gave the most useful results, and it was found that members of the groups differentiated by the animal tests did, in general, react similarly with the various carbohydrates and glucosides.

D. G. H.

Indian Tea-Fungus. E. Dinslage and W. Ludorff. (*Z. Unters. Lebensm.*, 1927, **53**, 458–467.)—Indian tea-fungus is composed of *Bacterium xylinum* and acid-resisting yeasts, and is used for the preparation of kvass, which is in general use throughout Russia and elsewhere as a beverage and as a cure for constipation. In England it is employed for making household vinegar. When it is grown in a weak infusion of tea containing sucrose, the sugar undergoes inversion and fermentation, the colouring matter of the liquid is largely precipitated with the yeast cells, and the nitrogenous substances of the infusion become degraded to amino-acids and ammonia. The acids formed consist of acetic and lactic acids, to which the dietectic value and healing properties of the product are due. Injurious properties are not to be feared unless the fermentative changes are allowed to proceed too far or vessels of non-resistant metal are employed in the manufacture. The infusion of tea may be replaced by one of coffee. T. H. P.

Toxicological and Forensic.

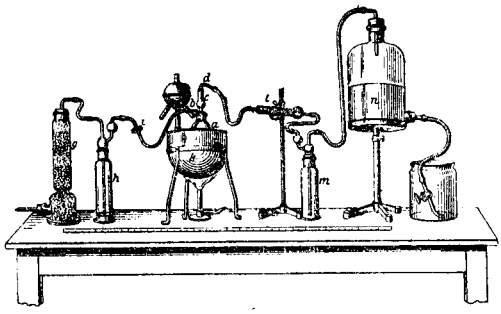
Determination of Very Small Amounts of Yellow Phosphorus in Red Phosphorus. R. H. Kray. (*Ind. Eng. Chem.*, 1927, **19**, 816.)—The test depends on the reaction between yellow phosphorus and copper sulphate in the presence of carbon disulphide. Strips of filter paper are dipped in 10 per cent. copper sulphate solution and then dried ; when this paper is immersed in a solution of yellow phosphorus in carbon disulphide and then dried quickly, a brown coloration is obtained. To test red phosphorus for the presence of yellow phosphorus, 20 grms. of the sample are treated with 30 c.c. of carbon disulphide, and the solution is kept in the dark for twenty-four hours and filtered. Fifteen c.c. of the filtrate are tested with the prepared paper ; if the concentration of the yellow phosphorus is not high, the solution is evaporated, measured and tested at intervals. At the stage at which a coloration is obtained on the paper the colour is compared with that produced by a known amount of yellow phosphorus under similar conditions. The test will detect as little as 0·003 per cent. of yellow phosphorus in red phosphorus. W. P. S.

Cadmium as a Coating Metal for Domestic Utensils. A. Gronover and E. Wohnlich. (*Z. Unters Lebensm.*, 1927, **53**, 392–396.)—The technical uses of cadmium and its alloys and its physiological effects (which are similar to those of zinc), are briefly reviewed. On account of its clean appearance and resistance to oxidation, cadmium has recently been used to coat cooking and

drinking vessels and cutlery, and to protect iron articles from rust. The solubility of cadmium in solutions of dilute acetic acid (0·5 to 2·5 per cent.) is greater than that of zinc, and increases with the period of contact, rapidly at first, and then attains an almost constant value. It is almost independent of the strength of the solution, whereas that of zinc increases markedly with the concentration. For both metals similar effects have been observed with hot acid, but in each case the solubility of cadmium was the higher. Plum jam left in contact with a stick of metal coated with cadmium for three days was found to contain 15 mgrms. of cadmium per 50 c.c. J. G.

Organic Analysis.

Determination of Water in Organic Substances by means of Calcium Carbide. A. Cantzler and S. Rothschild. (*Z. Unters. Lebensm.*, 1927, **53**, 425–435.)—In the apparatus shown, the flask *a* of about 50 c.c. capacity is fitted



with a ground stopper carrying a gas-delivery tube *b* and a drying tube *c* filled with granular calcium carbide over a plug of glass wool and fitted with a ground tubular stopper *d*. The substance (about 3 grms.) is weighed in the dry flask, into which is introduced a 5 c.c. beaker *f* containing 5 grms. of calcium carbide. The flask with its contents, and closed by the glass-plugged rubber tubes *e* and *e'* is weighed, and is connected at *d* with a calcium chloride tube and thence with an aspirator by means of which air may be drawn, by way of a tower containing alternate layers of calcium chloride and soda lime, and a wash-bottle containing concentrated sulphuric acid, through the apparatus. The tube *b* being shut off from the air dryers by a screw clip on the connecting tube, the beaker is upset and the carbide mixed with the substance. When evolution of gas slackens, the flask is heated in a bath of toluene or aqueous glycerol to a temperature depending on the nature of the material under examination and usually for 1 hour. After the bath is removed and the apparatus is cool, the acetylene is completely expelled by a slow current of air, the apparatus being finally weighed. According to the equation—$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$,—1 grm. of acetylene corresponds with 1·385 grms. of water, but, owing to absorption of small quantities of water by the calcium hydroxide, a loss in weight of 1 grm. actually corresponds with

1·443 grms. of water. The values calculated on this basis agree well with those actually obtained by drying in a vacuum over phosphorus pentoxide. When, however, drying is carried out in air, the results yielded are in accord with those given by the above method, if use is made of the factor 1·385 instead of 1·443. The presence of organic acids, such as tartaric acid, does not affect the results given by this method. The calcium carbide cannot be replaced by aluminium carbide. T. H. P.

Volumetric Determination of Hydroxyl Groups in Sugars and other Organic Compounds. V. L. Peterson and E. S. West. *J. Biol. Chem.*, 1927, **74**, 379–383.)—The number of hydroxyl groups in many organic compounds can be rapidly and conveniently determined by treatment with acetic anhydride and pyridine, followed by titration, as suggested by Verley and Bolsing (*Ber.*, 1901, **34**, 3354, 3359.) The method has been used much less than its merit justifies, and only tested on a few compounds. Results are now given of determinations carried out on various hydroxylated compounds, especially sugars and sugar derivatives, with which the method works well. For a determination, 0·1 to 0·8 grm. of substance, depending upon the number of hydroxyl groups present, is weighed and placed in a Pyrex test-tube (16 × 150 m.m.), to which are added 3 to 5 c.c. of acetic anhydride pyridine mixture (1 volume of anhydride and 2 volumes of pyridine) accurately measured. A blank is prepared at the same time. The tubes are either corked and left at 37° C. in a warm room, or else fitted with Hopkins' condensers and heated in an electric air oven. Electric lamps in the bottom of a tin can, provided with a wooden cover perforated with holes large enough for the test-tubes, make a good oven. After acetylation is complete (24 to 48 hours at 60 — 80° C.) the product is mixed with approximately 200 c.c. of ice water and titrated to phenolphthalein with 0·5 *N* sodium hydroxide solution. Blank titration—sample titration = equivalent of acetyl bound by hydroxyl (1 c.c. 0·5 *N* NaOH = 0·0215 grm. CH_3CO and 0·5 m*M* hydroxyl). When the hydroxylated compound is an acid the titration values must be corrected by the amount of alkali neutralised by the quantity of acid used. The presence of pyridine does not interfere with the titration of acetic acid to phenolphthalein. Conditions of time, temperature, etc., may be varied for different compounds at the convenience of the worker. P. H. P.

Determination of Propionic Acid in Acetic Acid. F. Baum. (*Chem. Zeit.*, 1927, **51**, 517.)—The author condemns the method in which the mixed acids are converted into calcium, sodium or silver salts, the proportion of propionic acid being calculated from the percentage of base in the mixed salts. The method of fractional distillation is also rejected in the case of commercial 80 per cent. acetic acid, on account of the volatility of propionic acid in steam. The method recommended consists in oxidising the mixed acids with potassium dichromate and sulphuric acid and calculating the propionic acid from the amount of unreduced dichromate found by iodimetric titration. Under the conditions given below the propionic acid is oxidised to acetic acid and no further. The acetic

acid to be tested is diluted to about 2 *N* strength, and 25 c.c. of this solution are placed in a 300 c.c. round-bottomed flask, having a neck about 12 cm. long. Seventy-five c.c. of 0·25 *N* potassium dichromate solution are added, and, after mixing, are followed by the slow addition down the neck of the flask, of 70 c.c. of pure sulphuric acid. The flask is then gently shaken, one or two capillary tubes added to avoid bumping, and the mixed solution (already hot) is evenly and gently boiled beneath a reflux condenser for 3 hours (cork or rubber connections must be avoided). The colour of the solution should not change beyond a dark brownish tint. After cooling, the solution is diluted to 500 c.c., and 100 c.c. are added, by means of a pipette, to a solution of 1·5 grms of sodium iodide in a few c.c. of water and 10 c.c. of dilute (1:4) hydrochloric acid, and the liberated iodine titrated with 0·1 *N* thiosulphate solution. The difference between the volume of thiosulphate used and 37·5 (one-fifth of the total amount of dichromate expressed as 0·1 *N*) is a measure of the amount of propionic acid present. The sample should be tested qualitatively for formic acid; if present this must be determined by the usual methods, and an allowance made (0·0046 grm. of formic acid = 2 c.c. 0·1 *N* potassium dichromate solution). R. F. I.

Determination of Propionic Acid in Acetic Acid and Acetic Anhydride. F. Baum. (*Chem. Zeit.*, 1927, **51**, 538–539.)—By titration of an acetic acid solution containing propionic acid and correction of the result in accordance with the proportion of propionic acid determined by the method recently described (see preceding abstract), the percentage of propionic acid in the total anhydrous acid may be calculated.

To determine propionic acid in acetic anhydride, a weighed quantity of the anhydride is dissolved in presence of sufficient strong sodium hydroxide solution, and the liquid heated for a short time to cause saponification and diluted, when cool, to 2 *N* concentration. To ensure complete saponification, this solution is heated for an hour on a water-bath. Oxidation by dichromate is then carried out as usual. The results obtained in certain cases are somewhat inaccurate, but the method is valuable on account of its simplicity. T. H. P.

Salts of α-Linolic Acid Tetrabromide. A. T. Oreta and A. P. West. (*Philippine J. Sci.*, 1927, **33**, 169–176.)—α-Linolic acid tetrabromide was prepared from lumbang oil, by separating linolenic hexabromide from an ethereal solution of the mixed fatty acids brominated at −10° C., removing the excess of bromine from the residue, and treating it with cold petroleum spirit, which precipitated a mixture of linolic tetrabromides. These were separated from the oily (gamma) tetrabromide and oleic dibromide, and crystallised from 95 per cent. ethyl alcohol. The purified α-linolic tetrabromide melted at 112·3 to 114·3° C. Its salts were prepared by first converting the acid into the potassium salt, and treating an alcoholic solution of this with an inorganic salt, such as zinc chloride. The m. pt. and solubility in various solvents of the purified salts were determined, and the results are recorded as affording data for devising new methods for separating mixtures of various linolic tetrabromides. The following m. pts. were obtained:

zinc salt, 154·7° C., complete at 158·8 °C. ; calcium salt, 208·7°–213·4° C. ; strontium salt, 200·4°–206° C. ; barium salt, turned brown at 196·3° C., completely melted at 202·5° C.; sodium salt, 194·2°–201·1° C. The solubility tests indicated that ethyl, methyl, and normal propyl alcohols are good solvents for the sodium salt ; benzyl and normal propyl alcohols, for the potassium salt ; ethyl benzoate appears to be the best solvent for the zinc, barium, calcium, and strontium salts.

Determination of Oleic and Elaidic Acids in the presence of each other. J. P. K. Van der Steur. (*Rec. Trav. Chim. Pays Bas*, 1927, **46**, 409–413.)—The reaction of iodine solution with unsaturated oils, fats, and fatty acids in carbon tetrachloride solution results in the establishment of an equilibrium which is dependent on the temperature (*ibid.*, 1927, **46**, 278). In the case of elaidic and oleic acids, the equilibrium constants have the respective values 5·0 and 94·7, which differ so widely that it is possible to determine the proportions of these two acids in a mixture by ascertaining the value of the equilibrium constant. The presence of saturated fatty acids does not affect the result, unless the proportions of oleic and elaidic acids are so small that a large quantity of the mixture has to be weighed out for the determination of the equilibrium constant. The method is inapplicable when other unsaturated acids, such as linolic and linolenic acids, are present, but if the mixture contains only one acid with multiple unsaturation, like linolic acid, this may be determined from the iodine value and the content of saturated fatty acids, and allowance made for it (*cf.* Bertram, ANALYST, 1927, 489). Hitherto all equilibrium constants have been determined at 0° C., but at this temperature (which is preferable) the solubility of some fatty acids in carbon tetrachloride is too small, and the following values have therefore been determined at 19·5° C.:—Oleic acid, 26·3; elaidic acid, 2·0; linolic acid, 17·2; erucic acid, 28·7; and brassidic acid, 1·8. T. H. P.

Reaction of Chloramine with Fats. B. M. Margosches and M. Frischer. (*Chem. Zeit.*, 1927, **51**, 519).—*p*-Toluenesulphochloramide-sodium ($CH_3.C_6H_4.SO_2(NaCl)+3H_2O$) has been suggested recently as a substitute for iodine in analytical processes, especially for the titration of sulphite liquors. References in the literature are scanty and contradictory. Engfeldt states that chloramine has no action on fats, whereas Feibelmann declares that it saturates unsaturated fatty acids. The authors have made experiments in which they have allowed 0·2 *N* chloramine solution in water or methyl alcohol to act on alcoholic fat solutions for intervals of 5 to 30 minutes in both acid and in alkaline solutions. The amount of chloramine absorbed was measured by treating the excess with potassium iodide in acid solution and with arsenious acid in bicarbonate solution. The effects of numerous factors have been studied, such as choice of medium for the chloramine and for the fat, excess of halogen, time, temperature, concentration, and order of addition. This study shows that quite small alteration of these factors materially affects the amount of chloramine absorbed. But it is hoped that further experiments will lead to the successful replacement of iodine by chloramine in fat analysis. R. F. I.

Boa Constrictor Fat. R. H. Kerr. (*J. Amer. Chem. Soc.*, 1927, **49**, 2046–2047.)—A specimen of boa constrictor fat was prepared from the carcass of a boa constrictor which had died from natural causes. The rendered fat was a clear liquid of faint yellow colour and with a peculiar and somewhat unpleasant odour. When cold, it was a soft, yellowish solid. Its analytical values were: M. pt., 28·5°; iodine value (Hanus), 79·4; iodine value of liquid fatty acids, 113·1; n_D^{40}, 1·4619; sp. gr. at 100° C. (water at 15·5° C. = 1), 0·8629; saponification value, 196·8; and free fatty acids, 0·17 per cent. The unsaturated acids consisted of oleic acid, linolic acid and a highly unsaturated acid which formed an insoluble bromine addition product, tentatively identified as octobromostearic acid. The saturated acids consisted of palmitic and stearic acids. P. H P.

Kentucky Coffee Nut Tree Seed Oil. C. Barkenbus and A. J. Zimmerman. (*J. Amer. Chem. Soc.*, 1927, **49**, 2061–2064.)—The Kentucky coffee nut tree (*Gymnocladus dioica*), which is not a common tree, grows over an area extending from central New York westward to Minnesota and southward to the Tennessee line. A saponin and a toxalbumin are reported by Watson and Sayre (*J. Amer. Pharm. Assoc.*, 1917, **6**, 601) to be present in the seeds. The same authors report deaths from eating the unroasted seeds, but no references are given. An approximate analysis has been made of the seeds and pods of this tree. A clear, light yellow oil, practically odourless, and with a bland taste, was obtained from the seeds. The physical and chemical characteristics of this oil were as follows:—Sp. gr. at 20° C., 0·9219; n_D^{20}, 1·4769; iodine value (Hanus), 137·5; saponification value, 191·0; Reichert-Meissl value, 0·44; acid value, 0·39; acetyl value, 11·35; unsaponifiable matter, 1·28 per cent.; soluble acids (as butyric acid), 0·83 per cent.; insoluble acids, 93·93 per cent. (iodine value, 122·0); unsaturated acids (corr.), 89·74 per cent. (iodine value, 145·0); saturated acids (corr.), 4·86 per cent. (iodine value, 3·4, before correcting). A phystosterol with a constant melting point of 165°–166°C. has been isolated. The composition of the oil from the seeds is given as: Glycerides of oleic acid, 37·41; of linolic acid, 56·37; of saturated acids (probably stearic and palmitic acids with a small amount of arachidic acid), 5·08; and of unsaponifiable material, 1·28 per cent. The oil does not readily become rancid. P. H. P.

Detection of Lactic Acid in the Presence of Other Organic Acids. F. G. Germuth. (*Ind. Eng. Chem.*, 1927, **19**, 852–853.)—Lactic acid, or a solution of a lactate acidified with a slight excess of hydrochloric acid, gives an orange or purple coloration when mixed with 15 per cent. potassium thiocyanate solution, and the colour is not discharged on the addition of mercuric chloride solution. The reaction is not given by citric acid, tartaric acid, succinic acid, butyric acid, benzoic acid, salicylic acid, etc. If traces of iron are present a coloration may be obtained on the addition of the thiocyanate, but this coloration is at once discharged by the mercuric chloride. The reaction may be obtained with a 0·5 per cent. solution of lactic acid. W. P. S.

A Hydrolysis Number Determination for Wood Cellulose. L. F. Hawley and L. C. Fleck. (*Ind. Eng. Chem.*, 1927, **19**, 850–951.)—The following hydrolysis method is recommended for application to cellulose obtained from wood pulp by the Cross and Bevan chlorination process;—One grm. of the cellulose is heated for three hours on a boiling water-bath with 100 c.c. of 15 per cent. sulphuric acid, the insoluble residue then collected on a filter, washed with hot water, alcohol, and ether, dried at 105° C., and weighed. The loss in weight is termed the hydrolysis number. W. P. S.

Differentiation of Green and Mature Woods. G. Fron. (*Ann. Falsif.*, 1927, **20**, 386–391.)—In order to differentiate green and mature woods the sample is sawn into portions 2–3 mm. thick, dried to constant weight, and 10 grms. boiled for 10 mins. with 80 c.c. of distilled water, and the P_H value of the resulting solution determined. This, as a rule, decreases with the age of the wood, so that the state of the wood may thus be gauged, and wood dried in hot air and that aged in the yards differentiated. The following values were obtained for green and old woods :—

	Green.	Mature.		Green.	Mature.
Beech	6·0	4·6	Pear	5·6	4·4
Hornbeam ..	5·6	4·4	Epicea	5·2	4·6
Elm	6·5–6·7	5·2	Walnut	5·2	4·6
Service tree ..	5·0–5·1	4·2			

The method cannot be used for woods treated by carbon disulphide, acetic acid, etc., or for those that have been in sea water. If the wood is treated by ozonised air an oxidation may be produced in 1 or 2 months similar in character to that occurring when the wood is matured in the yards. D. G. H.

Inorganic Analysis.

Determination of Cadmium and Aluminium by Means of Oxyquinoline. R. Berg. (*Z. anal. Chem.*, 1927, **71**, (*a*) 321–331, (*b*) 369–380. *Cf.* ANALYST, 1927, 302, 431, 494.)—(*a*) Cadmium is precipitated, like zinc, from acid acetate (sensitiveness, 1 : 416,000) or alkaline tartrate (1 : 104,000) solutions. The greenish-yellow, air-dry precipitate is $Cd(C_2H_6ON)_2{\cdot}2H_2O$; dried at 100° C. it retains $1\frac{1}{2}$ H_2O, becoming anhydrous after prolonged heating at 120° to 130° C. The precipitate cannot be ignited without loss, due to the volatility of the oxide. The warm cadmium solution (100 c.c.) is treated with sodium carbonate till slightly turbid, a little acetic acid till clear, 3 to 5 grms. of sodium acetate, and a slight excess of 2 per cent. alcoholic or 4 per cent. acetonic solution of the reagent. The yellow colour of the solution readily shows the excess. The liquid is heated to incipient boiling, left to clear, and filtered through a porous glass crucible (Schott < 7). The precipitate is washed with warm, then cold water, and dried at 105° or 130° C. to constant weight. The bromimetric method, already described for zinc, is much more convenient. (1 c.c. 0·1 *N* Br = 0·001405 grm. Cd.). A

concentration of 5 per cent. in acetic acid requires a large excess of reagent for complete precipitation ; in 10 per cent. acetic acid, cadmium is no longer precipitated. It is separable from magnesium in 2 per cent. acetic acid, in which the magnesium complex is easily soluble. For the quantitative separation of cadmium from copper, the solution is treated with 10 c.c. of glacial acetic acid and 3 grms. of sodium acetate per 100 c.c. ; the copper is precipitated in the cold with a small excess of the reagent. The precipitate is filtered off and washed with hot water ; the filtrate is partially neutralised with sodium carbonate, for the precipitation of the cadmium. Mercury is not precipitated if the weakly acid solution is treated with a slight excess of potassium cyanide, made alkaline with sodium carbonate, and acid with acetic acid. The precipitation of cadmium from alkaline tartrate solution is carried out as that of zinc, but the alkali concentration should not exceed 10 to 12 c.c. of 2 *N* sodium hydroxide per 100 c.c. In this manner, cadmium is separable from bismuth, antimony, tin, and arsenic by double precipitation, and from aluminium and ferric iron by single or double precipitation.

(*b*) Aluminium is precipitated as crystalline, greenish-yellow $Al(C_9H_6ON)_3$; sensitiveness, 1 : 310,000 in acid acetate, and 1 : 178,000 in ammoniacal tartrate solution. No precipitation takes place in tartrate solution containing sodium hydroxide. The precipitation in acetic solution permits of separation from magnesium, alkaline earths, and alkalis : the cold, feebly acid solution (100 c.c.) is treated with 3 to 5 grms. of sodium acetate and, while being stirred, an excess of 2 per cent. oxyquinoline acetate. After warming to 70° C. the precipitate is collected, washed with a little hot, then cold water, and dried to constant weight at 110°C. ; aluminium factor, 0·0587 (acetate reagent : 3 grms. of the base are triturated with 3 c.c. of glacial acetic acid ; 100 c.c. of hot water are added, and dilute ammonia, drop by drop, till cloudiness sets in, and the liquid filtered). The aluminium complex is noticeably soluble in alcohol and in acetone. Ignition to the oxide must be carried out very cautiously under a layer of 3 to 5 grms. of anhydrous oxalic acid, the complex being rather volatile. For the bromimetric determination, which is always preferable, the washed precipitate is dissolved in warm 10 to 15 per cent. hydrochloric acid ; 1 c.c. 0·2 *N* solution = 0·00045 grm. Al. The precipitation from tartaric solution is carried out as follows :—The liquid (100 c.c.) containing enough tartaric acid to prevent precipitation of the hydroxide, and 5 to 10 grms. of ammonium chloride, is neutralised with ammonia, warmed to 70° C., and precipitated, drop by drop, with a small excess of 2 per cent. oxyquinoline acetate or 5 per cent. hydrochloride solution. An orange-yellow coloration of the liquor indicates excess. Strong ammonia (0·5 to 1 c.c.) is now added ; the liquid is kept hot for 5 minutes, left to clear, and filtered. A large excess of ammonium salts is immaterial, but much free ammonia interferes. For the separation of small amounts of aluminium (maximum 0·05 grm.) from much magnesium the solution (100 c.c.) is neutralised with sodium hydroxide till cloudy, cleared with acetic acid, and precipitated cold with 2 per cent. oxyquinoline acetate solution. After warming till the aluminium precipitate becomes crystalline, it is dissolved in dilute hydrochloric acid and titrated. The magnesium is

precipitated in the filtrate after it has been rendered ammoniacal. (ANALYST, 1927, 431.) To separate small amounts of magnesium from much aluminium, the solution (100 c.c.) is treated with 3 to 5 grms. of sodium tartrate and an excess of 15 c.c. of 2 *N* sodium hydroxide above the quantity required for neutralisation. A small excess of reagent is added in the cold, and the magnesium precipitate rendered crystalline by warming. It is collected after cooling, washed with faintly alkaline 1 per cent. sodium tartrate solution, and titrated bromimetrically. W. R. S.

Confirmatory Test for Aluminium. W. J. Allardyce. (*J. Amer. Chem. Soc.*, 1927, **49**, 1991.)—A modification of the test proposed by Atack (*Chem. Zentr.*, 1916, [1], **82**, 176) is suggested which has the advantage that the reagent (a saturated solution of alizarine in concentrated acetic acid) need not be freshly prepared each time; also the colour absorption is greater. The aluminium hydroxide is separated from any chromium and zinc, washed, dissolved in hydrochloric acid, and then reprecipitated with a slight excess of ammonium hydroxide. One drop of the alizarine reagent added to this solution imparts an apple-blossom pink coloration to the aluminium hydroxide, which soon settles out and leaves a colourless solution above. P. H. P.

Thioglycollic Acid as a Colour Test for Iron. E. Lyons. (*J. Amer. Chem. Soc.*, 1927, **49**, 1916–1920.)—Thioglycolic acid is recommended as a delicate colour test for iron; it is more delicate than the usual thiocyanate test, and will detect iron in dilutions up to 1 : 10,000,000. The test is independent of the state of oxidation of the iron, for it is given equally well with either ferrous or ferric iron, whilst the thiocyanate test is sensitive only to ferric iron. The mechanism of the reaction is discussed. The reagent is really a test for ferrous iron, but, as it promptly reduces ferric iron to the ferrous state, it forms a general test for ionic iron. Since the thioglycolic acid test is applied in ammoniacal solution, a condition under which the colour obtained with ferric iron and thiocyanate is completely discharged, the thiocyanate test may be applied first of all to the same solution. The thioglycolic acid test is applicable quantitatively in dilutions which approximate 1 part of iron in about 5 millions. This, in conjunction with the thiocyanate test, forms a simple colorimetric method for the determination of both ferric and ferrous iron in the same solution. Thioglycolic acid and ferrous iron in ammoniacal solution produce a red or purple colour which is pink in dilute solutions. The delicacy of the reaction was not affected by the following substances (0·01 grm. per c.c. of 1 : 500,000 ferric solution) : Sodium acetate, arsenate bromide, benzoate, citrate, cacodylate, chloride, fluoride, glycerophosphate, iodide, phosphate, pyrophosphate, salicylate (with 3 or 4 drops instead of one), sulphate, sulphite, sulphocarbolate, thiosulphate, etc., nor by the salts of the following metals : potassium, lithium, barium, calcium, strontium, and, if not in too large amounts, mercury, copper, cadmium, zinc, tin, magnesium, silver, bismuth, etc. When these latter are present in the order of the concentration of the iron no interference is observed. Large amounts (0·001 grm. per c.c. or more) which of themselves give a colour with the acid or tend to precipitate

with aqueous ammonia may affect the delicacy of the test. The addition of sodium citrate will often in such cases bring out the full colour due to the iron present. P. H. P.

Determination of Potassium in Potassium Iodide. F. S. Hawkins and J. R. Partington. (*J. Chem. Soc.*, 1927, 1397.)—The authors condemn the methods at present in use for determining potassium in the presence of potassium iodide, namely the cobaltinitrite and the chloroplatinate, and also the perchlorate method by evaporation to dryness. The method recommended is as follows :— Saturated solutions of sodium perchlorate, and also of potassium perchlorate, are made in 96 per cent. alcohol, cooled to 0° C., and filtered. The alkali iodides are dissolved in the alcohol saturated with potassium perchlorate, an excess of the alcoholic solution of sodium perchlorate is added, the mixture boiled, cooled to 0° C., and filtered through a Gooch crucible. The precipitate is washed with the alcohol saturated with potassium perchlorate at 0° C., dried at 360° C., and weighed. This method gave results of the order of 99·95 per cent. accuracy. R. F. I.

Physical Methods, Apparatus, etc.

New Method of Quantitative Analysis Applicable to a Mixture of the Rare Earths. E. Delauney. (*Compt. rend.*, 1927, 185, 354–357.)—Since the size of the absorption bands of a solution of a rare element depends solely on the number of atoms encountered by the incident ray of light, (Beer's Law), the concentration (x) of rare earth in a solution may be calculated from the depth of liquid (E) required to produce an absorption band equivalent to that produced by the depth (e) of a solution of known concentration (C), from the formula $x = C.E/e$. The method has been applied to solutions containing neodymium or praseodymium, or both, in neutral and in nitric acid solutions, and involves an error of less than 0·05 per cent. The high value of the magnetic susceptibility of dysprosium has also been confirmed as a result of the study of the rare earth fractions of this element. J. G.

Ignition Points of Gases in Nitrous Oxide. H. B. Dixon. (*Lancet*, 1927, **212**, 247–248.)—Contrary to the opinion expressed by Humphrey Davy, hydrogen, ethylene and propylene have lower ignition points in nitrous oxide than in oxygen ; such ignition points are lower than the temperature at which thermal decomposition of the nitrous oxide is appreciable. With hydrogen there is a crucial pressure (about that of the atmosphere), above and below which the ignition point of the gas in nitrous oxide falls. For ethylene this crucial pressure is about 500 mm., at which ethylene ignites within 0·5 second at 605 °C. At atmospheric pressure ethylene ignites rapidly at 592° C., which is only 14° C. below the ignition point in oxygen, but when the mingling gases are in contact with a heated surface the difference between the ignition points in the two cases is more marked. At ordinary pressures propylene ignites, both in oxygen and in nitrous oxide, at lower temperatures than ethylene under the same conditions, but at low pressures the ignition of propylene in nitrous oxide sometimes occurs

at a higher temperature than that of ethylene. The crucial pressure for propylene is about 200 mm. lower than that for ethylene, but otherwise the ignitions are governed by the same general rule. T. H. P.

X-Ray Examination and Structure of Textile Fibres. G. R. Levi. (*Giorn. Chim. Ind. Appl.*, 1927, **9**, 269–275.)—A summary is given of the knowledge obtained of the internal structure of cellulosic fibres, starch granules, rubber, etc., as a result of the X-ray examination of these substances. T. H. P.

References to Scientific Articles not Abstracted.

EXPERIMENTAL RESEARCHES ON THE NATURE OF THE BACTERIOPHAGE. By CARL PRAUSNITZ. *Lancet*, 1927, 213, 535 (Sept. 10).

D'Herelle's observations and views—Is the bacteriophage derived from the bacterial cell?—Or from the human (or animal) host?—Is the bacteriophage a living ultra-microbe?—Size of the phage corpuscles—Random variability—Variability in a definite direction—The facts point to the bacteriophage being a living organism.

ALCOHOLIC CONCENTRATION IN URINE AS A TEST OF INTOXICATION. By G. CARTER. *Brit. Med. J.*, 1927, 333 (Aug. 27).

Definitions of intoxication—British Med. Assoc. Committee's definition: "Loss of power of delicate nerve control from indulgence"—Recognised tests—Analytical tests—Difficulties—Safeguards against fermentation of glycosuric specimens—Comparison of analytical results with clinical observations. (*Cf.* ANALYST, 1926, **51**, 208.)

THE STOCKHOLM PAPYRUS. By E. R. CALEY. *J. Chem. Education*, 1927, **4**, 979 (August).

History of the Egyptian papyrus known as the Stockholm Papyrus—First translation of the Greek into English—Commentary on the 154 recipes—Proof that the purple of the ancients was not obtained exclusively from shellfish.

PYREX AS A CONTAINER FOR RADIUM SOLUTIONS. L. F. CURTISS. *Nature*, 1927, **120**, 406 (Sept. 17). (Communication from Bureau of Standards, Washington.)

Unsuitability of pyrex vessels for radium salt solutions—Cracking of the interior surface—Result of bombardment with α-particles—Quartz similarly affected.

Reviews.

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Volume V. Edited by S. S. SADTLER, E. C. LATHROP and C. A. MITCHELL. Pp. xii+700. London: J. & A. Churchill. 1927. Price 30s. net.

In this age of specialisation even the specialist has to rely, more and more, on books for a large part of his knowledge. The task of compiling the necessary comprehensive treatises in the many branches of chemical science is obviously a difficult one. Allen's *Commercial Organic Analysis* is, to quote from its full title, "a treatise on the properties, modes of analysis, and proximate analytical examination of the various organic chemicals, and products employed in the arts, manufactures, medicine, etc." The difficulties of marshalling the vast array of data, and presenting it in a convenient and readable form have been successfully overcome by the editors and contributors, who are to be congratulated on the result of their work.

Volume V. of the fifth edition, which is now published, is the work of five English and four American contributors. It covers a wide field, and will be of value to analytical (and other) chemists who are concerned with the leather industry, and the manufacture and use of inks of all kinds, intermediates for dyes, synthetic drugs and natural colouring matters.

The longest section, which occupies nearly a third of the volume, is that on "Tannins," by Dr. Nierenstein. This section has been largely re-written for the new edition. The conflicting views of Fischer, Freudenberg and Nierenstein regarding the constitution of the gallotannins are summarised, and there can be little doubt that the question is still an open one. The discovery by Mitchell of a gallotannin which contained no glucose is important, in view of the fact that glucose was believed by Fischer to be an essential constituent of the gallotannin molecule. Amongst a number of new tests here described, are the Goldbeater's Skin Test for tannins, which is claimed to be specific, and the rather elaborate series of tests devised by Ware for the qualitative analysis of the tannins. The latest official methods of the various European countries, and of the U.S.A., for the quantitative analysis of tannins are all fully described.

Leather chemists will also find the section on the analysis of leathers, by A. E. Caunce, to be a valuable collection of analytical methods.

Prof. Gardner's section on "Natural Colouring Matters" deals chiefly with indigo, and is notable for the detailed description of the methods evolved by Gardner, Green, Lloyd and Frank for the estimation of the indigo fixed in fabrics, dyed with indigo alone, and those "topped," or "bottomed" with other dyestuffs.

The section on "Colouring Substances in Foods" has been re-written for this edition by W. E. Mathewson (U.S.A.). It contains a comprehensive scheme for the isolation and identification of some 120 colouring matters. This scheme should be useful to others, as well as to the food analysts for whom it is primarily intended. In parenthesis it may be asked why the author uses the term "anthocyan," when "anthocyanin" is the accepted term. If this is an "Americanism," it is one of the very few that occur in this volume.

Other sections are concerned with Writing Inks (C. A. Mitchell), Amines and Ammonium Bases (H. E. Cox), Benzene and Homologues (J. B. Hill), Aniline and its Allies (A. B. Davis), Naphthylamines, Pyridine, Quinoline, and Acridine Bases (A. B. Davis).

Of these, the three last are intended to be introductory to the forthcoming volume VI, which is to deal with synthetic dyes. These sections are the weakest part of the volume. The contributors attempt to compress into the available space, not only the analytical methods, which are the main object of the book, but also methods of preparation and properties. The latter are necessarily very incomplete. Surely it would have been wiser to omit this information which is already available in very full detail in Beilstein's *Handbuch ?*

The volume, as a whole, is remarkably free from errors. Phenyl acetamide ($C_6H_5.CH_2.CONH_2$) is, however, described (pp. 568, 569) as being identical with acetanilide ($C_6H_5.NH.COCH_3$), and is indexed as such. There are one or two minor printing errors, such as *acetaniline* for *acetanilide* (table of contents), *Area*

for *Urea* (p. 270, footnote). The book is well indexed. and in this respect is an improvement on the earlier volumes. G. H. CHRISTIE.

NOSTRAND'S CHEMICAL ANNUAL. Edited by John C. OLSEN, Ph.D., D.Sc. Pp. 864 and Index. London: Chapman & Hall. 1927. Price 21s. net.

This most compact and useful book of reference has now reached its sixth edition, and has more than justified its existence, both by its reliability and by the variety of its contents.

To the analytical and consulting chemist it specially appeals, and there is probably no single volume of its kind which gives more useful and, indeed, indispensable data.

The subjects dealt with are mainly and necessarily arranged in the form of tables, of which there are over 200, and range from base utilitarian matters like 5-figure logarithm tables, gravimetric factors for analysis and standard specifications (U.S.) for sieves, to more exalted topics, such as the isoelectric points of proteins, isotopes and the electric potentials of the elements.

The physical constants of organic and inorganic substances occupy about 340 pages, and from four to five thousand substances are referred to. There are special tables dealing with the alkaloids (19 pp.), essential oils (19 pp.), and oils, fats and waxes (20 pp.). The section on specific gravities and vapour densities occupies over 150 pages and includes full tables for methyl and ethyl alcohol, all the common acids, and solutions of numerous commercially important salts.

The data under Thermochemistry are commendably full and include energy conversion factors, temperature equivalents, freezing points and freezing mixtures, and heats of formation and heats of combustion.

Finally, under the imposing title "Stoichiometry," are included scientific problems arising out of the relation between mass and weight, calculations for correcting specific gravities at different temperatures, and for barometric and thermometric measurements, and more or less commercial problems concerning the dilution and concentration of liquid mixtures.

In such a short résumé it is impossible fully to mention individually such a vast number of tables, but the value of the volume, as a whole, requires no further comment. Everything has been done to render it of practical use. The type is very clear, the ample table of contents and a full index make it easy to find the information wanted, and references to original sources are given throughout the text. CECIL H. CRIBB.

OIL ANALYSIS. By AUGUSTUS GILL, Ph.D., Sc.D. Eleventh Edition. Pp. viii+293. London: J. B. Lippincott Co. Price 18s. net.

The fact that ten editions of this book have been exhausted within the comparatively short span of thirty years is evidence of its popularity, and constitutes a tribute alike to the usefulness of the subject-matter and the skill and clarity shown in its presentation. This new edition—the eleventh—is, as the preface states, principally intended for beginners, and, as such, it fulfils its purpose admirably.

The book consists of a short preliminary chapter on the composition of the various oils and fats, four chapters on petroleum and its products, followed by a short description of the various tests to be applied to an oil in order to ascertain its purity; two chapters comprising a description of the various oils and fats and the sources whence they are obtained; a chapter on waste oils and fats, and a chapter on the examination of an unknown oil complete the book.

The chapters on petroleum and its derivatives are easily the best and most useful in the book. The methods used in the examination of a mineral oil are principally physical and designed to show if an oil fulfils certain specified requirements. As these tests only require care in their carrying out and furnish an unequivocal answer, they may legitimately fall within the province of the engineer, whereas it may be doubted if the engineering student can afford sufficient time to acquire the discrimination and judgment necessary to interpret the results obtained in the course of an examination of an oil or fat. Emphasis on this point is all the more necessary, since to-day so many tests are standardised down to the minutest detail that there is a tendency to regard the indications given by them as sacrosanct.

The section on petroleum products, although confined almost entirely to American practice and apparatus, may yet be of use to the English student. It is concisely and clearly written and is thoroughly up-to-date. It is quite refreshing to find a writer with the authority of the author of this book condemning as unnecessary the legion of the—mostly expensive—friction machines.

Turning to the section on fatty oils, this cannot be said to be quite so satisfactory. As might be expected, the attempt to compress so large a subject into the compass of a few chapters results in some loss of clarity. As before, the tests described are mainly the official American methods, and call for little comment, although exception may be taken to the practice of measuring iodine and bromine solutions with a burette, as also to the use of a burette in the determination of the specific gravity. The practice of boiling a solution of alcoholic potash without at least an air condenser cannot be commended.

There is given on p. 171 a surprising table showing the prices of a number of oils, in which lard, tallow and cottonseed oil are shown as cheaper than whale oil, and olive oil is shown as cheaper than sesame oil.

The book contains a fairly comprehensive array of tests; notable omissions are the precipitation of the sterols by means of digitonin, the determination of the acetyl value in the examination of castor oil, and the determination of the oxidised acids in blown oils. The method for the determination of glycerol might also with advantage be given.

The book is well "got-up," and is very free from misprints, only two being found. In the first chapter "palm oil" is used where obviously "palm-kernel oil" is intended, and, later, the temperature to which linseed oil must be heated in order to precipitate the mucilage is given as 30° C. instead of 300° C.

In spite of these strictures, the book can be recommended. The student who has worked through it will have gained, in addition to considerable manipulative skill, at least a wholesome appreciation of the difficulties which beset the analyst.

G. H. WARBURTON.