SEPTEMBER, 1937 Vol. 62, No. 738

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Death

With great regret we record the death, on July 26th, of William Jefferys Lesley, who had been a member of the Society since 1930.

Flour Spoilage

By D. W. KENT-JONES, Ph.D., B.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, April* 10, 1937)

Introduction.—When the chemist who specialises in the examination of flour is asked to make a report, it is usually with the object of assessing the value of a sample for the particular purpose for which it is intended, such as the making of bread under a specified fermentation system, or the manufacture of cakes, biscuits, and the like. It is well known that wheats of various origin, when milled, may give flours of very different qualities for breadmaking and so on, so that, although a flour may be quite sound and wholesome, it may not have the desired characteristics when made into a dough. The examination of flour for bread-making has become a specialised matter, involving both chemical and physical tests, and the use of expensive dough-testing apparatus.

In this paper, however, I am not dealing with these specialised problems, but with general faults concerning the wholesomeness and palatability of the flour, which render it unsuitable for general use. I have attempted to consider these faults under the term "flour spoilage" and to give examples of the more common types. Fortunately they are comparatively rare, when we consider the large amount of flour produced.

Taints.—Flour particles are extremely small (being dressed through "silks" with meshes ranging from 100 to nearly 200 to the inch), and hence the surface is very great as compared with the volume. Owing to this fact flour will readily

become tainted through the absorption of any odours in its vicinity and, although out-of-condition and unsatisfactory flour, or flour that has been spoiled, is not common, yet when this trouble does arise, it is generally due to the presence of taint. The taint, however, may not have been acquired subsequent to the making of the flour, but may be due to the fact that the wheat from which the flour was made was tainted and unsatisfactory. The commonest of these taints is probably "mustiness," and "mustiness" may certainly be due to the wheat itself being out of condition when it was ground into flour. English wheat that has been stored for a long time under unsatisfactory conditions may impart a musty taint to the flour. For example, if the wheat is kept from harvest until the spring of the following year, it sometimes develops "must," which taints the flour. "Out-of-condition" English wheat is not rare in the spring, but as a rule it is noticed and not ground into flour. "Mustiness" is often associated with a high mould count, but there has not been, to the best of my knowledge, sufficient work done for a dogmatic statement to be made on this point, for undoubtedly there have been musty flours with low mould counts. Whether or not such flours have once had a high mould count cannot be ascertained. Normally, however, the mould-content of flour tends to increase on storage, whilst bacterial contamination usually decreases.

All wheat contains foreign seeds, which are normally extracted in the cleaning process preparatory to milling, but sometimes they escape and are ground up in the flour. Most of them are harmless, but some will cause taint. A well-known example is the seed of *Melilotus*, which gives a sweet, hay-like flavour to the flour, and failure to eliminate this has caused serious trouble in the past. The *Melilotus* seed, which is very small and brownish-yellow, is often present in wheat from Russia and the Argentine. If *Melilotus*, of which there are several varieties, is present in wheats grown in hot countries, it is less likely than the *Melilotus* from temperate climates to cause taint. When wheats contaminated with these seeds are used, great care in cleaning is necessary, and the wheats must not be warmed or damped, as is done in the conditioning process preparatory to milling, until these seeds are removed, or the taint may become diffused and so be absorbed by the grain itself.

Other taints sometimes encountered are the odours of apples, oranges, phenols, and so on, which have been acquired during transit. For instance, I have known flour sent from Australia acquire the odour of apples, owing to its being loaded in a ship containing also a consignment of Tasmanian apples. Almost any taint may be acquired in this way, and the variety is at times startling. The odour of eucalyptus, due to the presence of eucalyptus leaves in the wheat, is occasionally encountered, especially in Australian flour.

Sometimes wheat becomes hot on storage and the grains have an incipient charred appearance. They are termed "bin burnt," and such grains often have a distinctive hot taste. This may result in the flour, subsequently milled from it, having a dull colour and the same unpleasant flavour. Wheats that heat in the stack are the usual cause of "bin burnt" grains.

It is not always appreciated that the baker is likely to experience trouble with tainted flour, even when the analyst may think the taint is almost too slight to worry

about. It is distinctly difficult to test for taint in flours that are only slightly affected. The best way, of course, is the simple procedure of making the flour into a smooth paste with cold water and scalding by the addition of boiling water. A sensitive nose, however, is required. The baker has a much more effective test. As soon as he opens the door of his oven after baking, volumes of steam roll out and, if there is any taint in the flour, it is perceptible in the steam from the bread and is very pronounced. In other words, the test that we apply is the same test as the baker's, but it is made in a very much less effective manner.

OTHER POSSIBLE DEFECTS DUE TO STORAGE.—Difficulties connected with the moisture-content of the flour may arise, but it is outside the scope of this paper to deal with loss of weight in storage (usually only of importance in small bags of self-raising flour) which is dependent on the vapour pressure of the flour and the relative humidity of the air in which it is stored.

On the other hand, if a flour has a high moisture-content and it is stored under pressure, as, for instance, when bags are piled up on top of one another, and particularly if the temperature is warm, as in the hold of a ship, hard lumps may form. This phenomenon is connected with the "respiration" of the flour. Such flour becomes completely unsatisfactory for ordinary purposes, and I have seen lumps fully a foot in diameter taken out of bags. Some bags set almost like cement. This is due to the flour having too high a moisture-content and being stored under the unfavourable conditions I have indicated. If such flour is re-ground and dressed, and provided that any lumps that contain discoloured pieces are discarded, it is often possible to re-mix it in small proportions with normal flour.

Sometimes flour becomes markedly acid on prolonged storage, but only if there are unfavourable conditions, such as excessive warmth and high moisture-content. Rancidity is also known, but is comparatively rare.

Damage due to sea water is, of course, well known, and I would draw special attention to the paper on the subject by Seaber (ANALYST, 1936, **61**, 14).

PESTS.—Troubles due to actual pests are also rare and are more common with wheat than with flour. The main trouble in this respect is due to the flour mite (*Acarus farinae*), and this, again, is more prevalent when the flour has a high moisture-content and has been stored in a warm place. No flour is sterile as regards either bacteria or insect eggs and, if the conditions are favourable, the latter will hatch and the insects multiply unduly. The appearance of the flour mite under the microscope is well known. Flour badly infested with mites becomes almost purple in colour, owing to the presence of thousands of mites and, if the flour is flattened with a spatula, the surface rapidly becomes uneven and rough as the result of the movements of the insects. Such flour, of course, cannot be used for normal purposes and has usually to be thrown away, although it is sometimes mixed with offals. This practice may also cause trouble.

The Mediterranean flour moth is a troublesome pest in the mill, but is only rarely met with in the finished flours. It is conceivable, however, that, if there were a burst in a "silk," one might find in the flour a matted mass of caterpillar silk. The moth lays its eggs in crevices, and the caterpillars are hatched in four to fourteen days. These caterpillars spin large quantities of a silk which becomes encrusted with the flour dust, and these masses may choke the mill. The duration

of the caterpillar stage may be several months. The moth causes sufficient trouble to make it necessary to fumigate mills with hydrogen cyanide, ethylene oxide or the like.

I have known mills to be infested with *Niptus hololeucus*, cadelle, *Tribolium confusum*, and mill worm, and there is always the danger of contamination of flour with rat and mice droppings. The fact that the flour is sifted through silks before being sacked generally means that, if such extraneous matters are found, the flour has become contaminated after leaving the mill. If flour has been badly contaminated with rat or mice dung it is, of course, likely to have a high bacterial population and particularly a high *B. coli* and *B. perfringens* count.

Attention should also be drawn to possible damage by the wheat bug (*blé punaise* or *Weizenwanze*); this seems to be mainly restricted to Central Europe, Persia, Syria and Morocco. There are a number of such wheat bugs, but the principal ones are *Eurygaster maurus*, *E. intriceps*, *Aelia rostrata* and *A. acuminata*. Grain thus damaged has a minute puncture surrounded by a yellow patch. Although the bug itself is seldom, if ever, met with in flour, the result of its attack is that the flour acquires excessive proteolytic activity, so that, when made into a dough, it becomes sticky and often unusable. The presence of only three per cent. of infected wheat can cause very serious damage. The examination of flour for this damage requires expert knowledge and is often carried out with the aid of special dough-testing apparatus, operating on fermenting doughs. If, however, the gluten from infected flour is washed out and allowed to stand under water for 1 to 2 hours, it shows a great tendency to "run," and loses its elasticity.

OTHER TYPES OF FLOUR SPOILAGE.—I have not attempted to deal with every possible type of flour spoilage. There might, for example, be trouble from the presence of ergot in flour, if the wheat from which it is made contains a sufficient quantity of the parasite and this has not been removed in the cleaning process. This is so rare in England and, indeed in most countries, that I have never had an example sufficiently pronounced to cause any trouble or difficulty, but the possibility always exists (*cf.* Barger, ANALYST, 1937, 352).

Trouble also arises sometimes from coloured spots in bread, and it is claimed that this may be due to discoloration in the flour. Numerous suggestions have been made to account for this, such as the presence of cow wheat (*Melampyrum arvense* L.), which, when ground, is said to yield a blue mass, the presence of blue stones, etc., but in practically every case the trouble is due to the presence of copying-ink pencil. A pencil may have been dropped into the wheat in milling, and have become powdered by the rolls, or a copying-ink pencil may have been sharpened in proximity to the stored flour and the minute particles thus produced have been picked up by the sack. If the former happens, the silks naturally do not sift out the minute specks and, when the flour is wetted for dough, the methyl violet spots spread and stand out. They can be seen in the dough and bread, and are easily identified. The stain dissolves readily in alcohol, and a low-power microscope usually reveals the presence of particles of graphite. The stain can be absorbed on a filter-paper, and the dyestuff may be identified by adding reagents such as potassium nitrite in dilute acetic acid (which changes the colour from violet to blue) or stannous chloride in hydrochloric acid, which turns the violet to green.

"Rope" is a disease which may develop in bread on storage. In the first place the bread develops yellowish-brown, slightly sticky, spots. At the outset the odour is only reminiscent of slightly over-ripe fruit, but it gradually becomes worse, and may sometimes be extremely repugnant, while the loaf itself may become a putrefying mass. The disease is due to the presence of bacteria of the *Mesentericus* group, mainly *Mesentericus vulgatus*. These are spore-forming organisms, and the spores are always present even in the best and purest flour. Provided, however, that their number is not excessive and that the conditions of bread storage are normal, the bacteria are not likely to multiply and, hence, the trouble will not arise. The spores, of course, resist the heat of the oven and, if the bread is stored under warm and moist conditions, and particularly if the yeast fermentation has been slow and sluggish, the trouble may develop. The spores then turn into the vegetative forms and rapidly multiply. At one time it was thought that the trouble was mainly due to flour that was too "ropy" or to lack of cleanliness in the bakehouse. While both these causes may aggravate the trouble, outbreaks arise only when bread is stored in a warm condition for too long periods, and then only if the bread has been made with a rather slow and insufficiently vigorous fermentation. If ropy bread appears it should, of course, be immediately destroyed and every precaution taken to prevent the bacteria from multiplying. Fortunately, *Mesentericus vulgatus* cannot exist in an acid medium, and it is therefore helpful to wash out all the troughs and other vessels with acid, such as vinegar, and even to incorporate acid substances, such as vinegar or acid calcium phosphate, in the succeeding doughs. Above all, the bread must be rapidly cooled, as then no difficulty is likely to arise. Hence, one-pound loaves, which cool more rapidly than four-pound loaves, may escape the trouble, whilst the larger ones are affected. Loaves should not be heaped together so that they cool slowly, and wrapping before cooling is also bad practice. The trouble, of course, comes only in hot weather. In warm climates there is often serious trouble from rope, which in England is rare. Practically all bread, especially if fermentation has not been vigorous, will develop rope on storage under conditions of warmth. I should like to emphasise the fact (*cf.* Amos and Kent-Jones, ANALYST, 1931, **56**, 572) that if the dough is made with a vigorous yeast fermentation, there is always less likelihood of trouble arising than if the fermentation is slow and sluggish. As a matter of fact, it is difficult to cause rope to develop to a pronounced extent in bread made with cool doughs and plenty of yeast.

THE LABORATORIES
CHARLTON GREEN
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The Volumetric Determination of Mercury

By M. FITZGIBBON, A.I.C.

THE work here described was undertaken to ascertain the most suitable method for determining mercury in organic compounds or in mixtures such as seed-disinfecting preparations.

A brief survey of well-known procedures for determining mercury shows that they may be classified as follows:—

(1) Reduction to mercurous chloride and separation of that salt prior to the final titration.

(2) Reduction to the metallic state.

(3) Direct method with potassium iodide in neutral mercuric salt solution.

(4) Acidimetric method, based upon the non-ionisation of mercuric cyanide.

(5) Determination with thiocyanate, directly in mercuric salt solutions or indirectly, as a zinc complex, involving separation and subsequent titration with iodate in strongly acid solution.

Of these methods, Nos. 1, 4 and 5 may be ruled out as unsuitable on account of being too tedious; method No. 3 can be used only with a neutral and pure solution of mercuric chloride; No. 5 is unreliable in the presence of chlorine or nitrogen oxides. The remaining procedure (No. 2), due to Rupp,[1] whilst excellent in theory, is liable to yield wholly unsatisfactory results, owing to some of the metal not reacting after the addition of iodine; this is due to the tendency of the reduced mercury to aggregate.

The addition of gelatin has the remarkable effect of retaining the reduced mercury in a stable "colloidal" suspension—in fact, so reactive is the metal in this state that it is almost possible to titrate directly with iodine, instead of adding an excess and back-titrating with thiosulphate. The presence of large amounts of alkali sulphate, chloride or nitrate has no influence upon the physical condition of the mercury, and interference by most substances, except such obvious ones as cupric salts (reduced by formaldehyde) and substances capable of being oxidised by iodine in acetic acid solution, need not be anticipated. The presence of cyanide does not affect the determination, and the procedure is, therefore, suitable for mercuric cyanide.

The improved method is as follows:—The mercuric solution resulting from the destruction of the organic mercurial preparation by any of the methods suggested below, is passed through a Gooch filter if there is any considerable quantity of insoluble matter (talc and silicious residues, present as "carriers" in seed-dressing compositions, remain after the preparation has been treated with sulphuric acid). The filtrate is treated with sufficient potassium iodide (about 1 g.) to form the soluble double salt, and then rendered alkaline with 5 *N* sodium hydroxide solution (an excess of about 5 ml. being added), and heated to about 60° C. Two ml. of freshly prepared, warm 2·5 per cent. gelatin solution are added, and then, with constant swirling, 3 to 4 ml. of 40 per cent. formaldehyde solution.

Reduction is extremely rapid, and the solution assumes a sepia shade, which may not be quite so dark if less gelatin is employed; in the absence of the colloid the colour is grey. The reduced mixture is cooled to about 20° C., acidified with excess of acetic acid, treated at once with 25 ml. of $N/10$ iodine solution and stirred, and the excess of iodine is titrated with $N/10$ thiosulphate solution (1 ml. of $N/10$ iodine $\equiv$ 0·01003 g. of mercury).

The satisfactory working of this procedure depends to some extent upon the method of preparing the mercury solution; the following notes on this point will be found of assistance:—Simple aliphatic mercury halides such as the higher alkyl (*e.g.* propyl) mercury chlorides, ethanol mercuri-chloride and the like, readily decompose when heated with conc. sulphuric acid, yielding mercuric sulphate; since some sulphur dioxide is produced by the action of the acid upon the alcohol or carbon residue of the compound, the solution and washings must be oxidised. Addition of bromine water, with subsequent boiling to remove the excess, is a satisfactory method of oxidation and ensures that all the mercury is in the mercuric state. Readily volatile and stable alkyl compounds are more safely decomposed by making them react with pure bromine in a pear-shaped flask fitted with a ground-glass air condenser. The resulting mixture of mercuric bromide and brominated compounds is heated with sulphuric acid in the usual manner, care being taken to avoid loss of mercury by sublimation.

Heating aromatic compounds with sulphuric acid usually leads to considerable charring, and prolonged heating at high temperature is necessary before the solution becomes colourless. The addition of a few drops of conc. nitric acid, however, to the dark sulphuric acid solution effects rapid clearing.

The sulphuric acid solutions, after short and rapid boiling, are ready for the addition of potassium iodide prior to reduction in alkaline solution.

The following results are typical of those obtained with this modification of Rupp's method:

Mercuric Chloride.—The 25 ml. of solution taken was calculated to contain 0·1252 g. of mercury. The gravimetric determination gave 0·1244 g. and the volumetric method 0·1238 g. of mercury (= 99·52 per cent. of the gravimetric result).

Ethyl Mercuric Chloride.—The salt was purified by recrystallisation from alcohol, and quantities of (1) 0·303 g. and (2) 0·2014 g. were used for the determination. As the C–Hg linkage in this compound is remarkably stable, the following procedure was followed:

The weighed sample was transferred to a pear-shaped 200-ml. saponification flask fitted with a ground-glass air-condenser about 30 cm. long. Two ml. of conc. sulphuric acid were pipetted down the condenser and then 1 ml. of anhydrous bromine. The reaction was completed by carefully heating the flask over a Bunsen flame. After cooling, about 25 ml. of water were poured down the condenser, and heating was continued until the bromine had almost ceased to appear as drops in the tube. The liquid, which was still yellow, was washed into a 250-ml. beaker, made up to about 125 ml., and boiled until free from bromine, a few grains of silver sand being added and the beaker covered with a clock-glass. After cooling, excess of potassium iodide was added; this caused liberation of a trace of

free iodine, which was removed by adding a drop or two of thiosulphate solution. The liquid was then rendered alkaline with soda and treated as described above. The amounts of mercury found were (1) 75·14 (2) 75·70 per cent. Theory, 75·67.

It would appear that for compounds of this type a tolerance of ±0·50 per cent. of mercury must be allowed; a variation of 0·10 ml. in a titration in the second determination introduced an error of this order. With care, however, and if a 25-ml. burette graduated to 0·05 ml. is used, consistent results of a high order of accuracy should be obtained.

Commercial Seed Dressings.—The proprietary article examined was "Semesan," stated to contain 30 per cent. of hydroxymercuri-chlorophenol.

The sample was prepared for reduction as follows:—One g. was treated with 4 ml. of conc. sulphuric acid in the apparatus described above, the flask being rotated to ensure thorough mixing. The pasty, dark coloured mass was heated fairly strongly, during which process some mercury sulphate sublimed and collected upon the cooler parts of the flask. After cooling, 1 ml. of conc. nitric acid was added, and the flask was gently heated; this caused the liquid to be appreciably decolorised. About 15 ml. of water and a few drops of bromine were then introduced, to ensure complete oxidation of the mercury and to saturate any trace of organic nitro compounds which would otherwise absorb iodine. The mixture was heated to boiling for a few minutes, then cooled and diluted somewhat, before being transferred to the 250-ml. beaker and treated as described above. Owing to the higher salt-content, some of the gelatin separated in flocculent clots, but this did not prevent the mercury from being finely dispersed and reacting quantitatively with the iodine (*vide infra*). The amount of mercury found was 17·15 per cent., compared with 17·40 per cent. calculated to be present.

Application of a drop of sulphuric acid to the ground-glass surface of the reflux tube prevents troublesome "binding" due to mercury sublimates at the joint; washing of this part is also facilitated. If, owing to variations in the salt concentration of the solutions, the gelatin clots and adsorbs mercury as a precipitate, it is useless to continue the determination; this is unlikely to occur, however, if care is taken and, moreover, is readily observed.

I wish to express my thanks to Dr. A. M. Ward, of the Municipal College, Portsmouth, for examining the method.

Reference

1. E. Rupp, *Ber.*, 1906, **39**, 3702; Abst., Analyst, 1906, **32**, 128.

Lunevale Products, Ltd.
Queen's Mill, Lancaster

The Colorimetric Determination of Copper with Sodium Diethyldithiocarbamate in the Presence of Moderate Amounts of Iron

By T. P. HOAR, M.A., Ph.D., B.Sc.

The colorimetric determination of copper by means of the yellow compound formed with sodium diethyldithiocarbamate is described by Callan and Henderson,[1] who suggest the removal of interfering iron by precipitation as ferric hydroxide with ammonia. However, as shown by Toporescu,[2] Haddock and Evers[3] and Hammence,[4] some copper is carried down by the ferric hydroxide even under the best conditions. To avoid this error, Haddock and Evers[3] add citric acid and ammonia to the solution containing copper and ferric iron. Sodium diethyldithiocarbamate solution is then added; the iron does not react under these conditions, and the yellow compound formed with the copper is extracted with four portions of carbon tetrachloride, as suggested by Grendel.[5] In this way copper may be determined in the presence of 50,000 times as much iron by weight. McFarlane,[6] following Warburg[7] and Drabkin and Waggoner,[8] prevents the reaction of iron (up to 90 times the amount of copper) by the use of an ammoniacal pyrophosphate solution, and extracts the copper compound with amyl alcohol; according to Thatcher,[9] isoamyl alcohol is better.

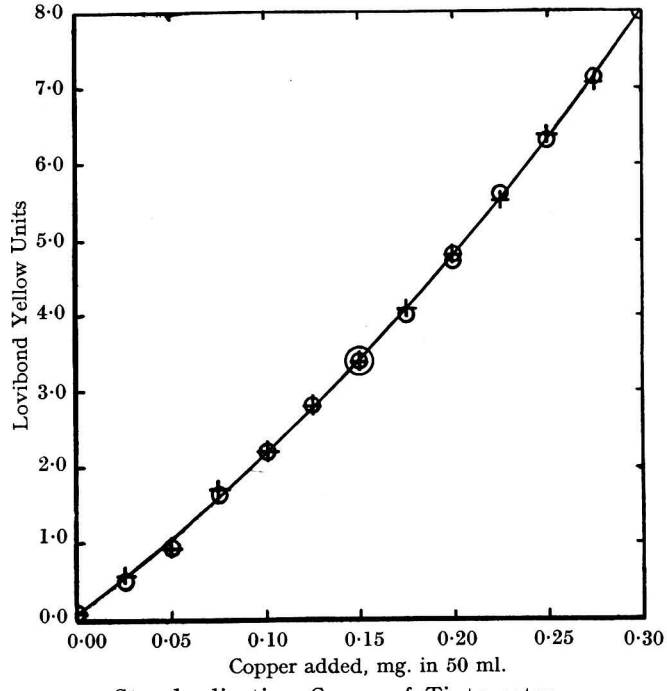
These extraction processes serve a dual purpose. First, the copper compound with sodium diethyldithiocarbamate is very sparingly soluble in water, all but the palest yellow solutions soon becoming cloudy and unsuitable for colorimetry, whereas it is readily soluble in organic solvents, giving suitable clear solutions; however, clear aqueous solutions may be obtained by the addition of a protective colloid, gelatin or gum tragacanth being recommended by Moseley, Rohwer and Moore.[10] Secondly, the yellow colour is separated from that due to ferric salts in the aqueous phase.

Since effective extraction may be very tedious, two methods of avoiding it when the iron present does not exceed about 100 times the amount of copper —a condition frequently encountered in practice—have now been devised. The first method is suitable for the determination of copper in the presence of some 25 times as much iron and a considerable amount of zinc. The second is suitable for larger amounts of iron, but is interfered with by zinc.

In the first method the iron is prevented from reacting with the sodium diethyldithiocarbamate by the addition of citric acid and ammonia, as in the procedure of Haddock and Evers.[3] A small amount of gum arabic is added and, on addition of the thiocarbamate, a clear golden-brown colour, excellently stabilised by the protective colloid, is obtained. The total yellow constituent of the colour is measured directly in a Lovibond tintometer. Any yellow colour due to ferric iron in the ammoniacal citrate solution is measured separately in another portion of the solution, to which all the reagents except the sodium diethyldithiocarbamate have been added. Subtraction of this small value from the total yellow colour value gives that due to the copper compound.

In the second method the iron is prevented from reacting by the addition of sodium pyrophosphate, as in the procedure of McFarlane,[6] but no ammonia is added; no yellow colour due to ferric iron then appears, and the colour subtraction process is unnecessary. Gum arabic and sodium diethyldithiocarbamate are added, and the yellow constituent of the aqueous solution is measured; exactly the same copper colour is produced as in the first procedure.

CITRATE METHOD.—*Solutions required.*—(1) Citric acid solution, 200 g. per litre; (2) ammonia, 100 g. per litre (1 vol. of ammonia of sp.gr. 0·880 to 2 vols. of water); (3) 1 per cent. gum arabic solution, prepared according to the directions of Zinzadze,[11] by dissolving at 50° C., cooling and adding 1 ml. of toluene per litre; (4) 0·2 per cent. sodium diethyldithiocarbamate solution. All reagents should be as free from copper as possible; the water should be condensed on silica or pyrex.



Standardisation Curve of Tintometer

Fig. 1

Procedure.—Place a 10- or 20-ml. aliquot portion of a suitably diluted solution (0·005 to 0·025 mg. of copper per ml.), containing any iron in the ferric state, in a 50-ml. flask. Add 10 ml. of citric acid solution (1), 8 ml. of ammonia (2) and 5 ml. of gum arabic solution (3), well mix, add 5 ml. of 0·2 per cent. sodium diethyldithiocarbamate solution (4), and make up to 50 ml. Measure the colour in a 1-cm. cell in a Lovibond tintometer, reading yellow units and using red and neutral tint for matching the tints only; this colour may conveniently be between 2·5 and 6·5 yellow units. Repeat with another 10- or 20-ml. aliquot portion, omitting the sodium diethyldithiocarbamate solution; this colour should not

exceed 0·6 yellow units. Obtain the yellow units due to the copper by subtraction and thence the copper from a standardisation curve such as that shown in Fig. 1. The circles represent points obtained by this method from copper solutions of known concentration.

Where rapidity is essential but the greatest accuracy is not required, the iron colour and the total colour may be measured consecutively in the same aliquot portion; the iron colour, without the copper reagent, is first measured, and then the total colour by adding 1 drop of a 2 per cent. solution of the reagent direct to the 1-cm. cell.

It is advisable to standardise any particular tintometer against copper standards containing all the reagents, to allow for local variations in lighting, and so on; the standard curve once obtained (*cf.* Fig. 1) automatically eliminates all blank corrections. Alternatively, the following table, obtained from the smoothed curve of Fig. 1, may be used to construct a large-scale curve, but the appropriate blank correction must be found for the reagents used.

TABLE I

Lovibond yellow units		Copper present mg. per 50 ml.
1·0		0·052
2·0		0·098
3·0		0·139
4·0	with	0·177
5·0	0·1 neutral	0·211
6·0	tint	0·244
7·0		0·275
8·0		0·304

Since the copper colour is a more reddish yellow than the iron, it is necessary to employ a colorimetric system, such as that of the tintometer, by which the amount of (arbitrary) yellow in each colour may be measured.

Test of the Method.—It was necessary to show that the colours produced by copper with sodium diethyldithiocarbamate and by ferric iron in ammoniacal citrate solution do not interfere with each other, and that ferric iron itself forms no colour with the reagent under these conditions. The effect of excess of nitrate, which may be present owing to its use in oxidising the iron or for other reasons, was also investigated. Various amounts of copper with different amounts of copper-free ferric iron (prepared from carbonyl iron) and potassium nitrate were taken in a total volume of 50 ml.; and the copper was determined by the colour subtraction procedure by an operator to whom the composition of the solutions was unknown. The results, in order of experiment, were:

Copper taken mg.	Iron taken mg.	Nitrate taken mg. NO_3'	Copper found mg.
0·26	2·3	46·5	0·27
0·62	1·6	25·5	0·62
0·38	0·0	87·0	0·37
0·21	0·8	64·0	0·20
0·84	0·4	17·5	0·83
0·50	0·5	0·0	0·51
0·40	10·0	0·0	0·39
0·25	2·5	2500	0·25

Evidently the colour subtraction procedure is valid, and a great excess of nitrate does not interfere. Haddock and Evers[3] mention that nitrate up to 0·75 mg. NO_3' in 50 ml. is permissible with their method; the present results indicate that far more may be tolerated.

Any nitrite present should be removed by making the original solution slightly acid with nitric acid, adding 0·5 g. of urea, and boiling the mixture for a short time.

Zinc, if present in large excess, may give rise to a turbidity; this can be prevented by making the solution more strongly ammoniacal, as in the original method of Callan and Henderson.[1] Arsenate does not interfere. As regards other interfering substances, the work of Haddock and Evers[3] should be consulted.

The copper colour is stable for at least 8 hours.

PYROPHOSPHATE METHOD.—*Solutions required.*—(1) Sodium pyrophosphate solution, 40 g. per litre of $Na_4P_2O_7$ dissolved in cold water; (2) 1 per cent. gum arabic solution; (3) 0·2 per cent. sodium diethyldithiocarbamate solution.

Procedure.—Place 10 or 20 ml. of the nearly neutral solution containing copper (0·005 to 0·025 mg. of copper per ml.) in a 50-ml. flask. Add 10 ml. of sodium pyrophosphate solution (1) and 5 ml. of gum arabic solution (2), well mix, add 5 ml. of sodium diethyldithiocarbamate solution (3), and make up to 50 ml. Measure the yellow units of the colour in a 1-cm. cell in a Lovibond tintometer. Read off the copper from a standardisation curve such as that shown in Fig. 1. The crosses represent points obtained from known copper solutions by this method.

It may be noted that the standard points obtained by the pyrophosphate method fall on exactly the same curve as those obtained by the citrate method for the reagents used in this work. It is best to construct a standardisation curve for any particular tintometer and reagents, or Table I may be used as before.

Since no colour subtraction is involved, any form of colorimeter is suitable. More dilute solutions (down to 0·0002 mg. of copper per ml.) can be dealt with by using a long tube of the coloured liquid.

Test of the Method.—Various solutions containing copper, ferric iron and nitrate were analysed, their composition being unknown to the operator. The results, in order of experiment, were:

Copper taken mg.	Iron taken mg.	Nitrate taken mg. NO_3'	Copper found mg.
0·58	10·0	0	0·59
0·40	7·5	55	0·39
0·32	12·0	0	0·33
0·38	10·0	500	0·38
0·90	0·0	250	0·88
0·60	5·0	100	0·60

Zinc gives a turbidity which can be avoided only by making the solution strongly ammoniacal; this gives a deeper colour due to ferric iron than that obtained by the citrate method, which is therefore to be preferred when zinc is present. Arsenate does not interfere.

The copper colour is stable for at least 8 hours. Very little change was observed after one day in a solution kept in a stoppered bottle.

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THE METALLURGICAL LABORATORIES
UNIVERSITY OF CAMBRIDGE

The Colorimetric Determination of Tin by Means of Toluene-3 : 4-dithiol ("Dithiol")

BY R. E. D. CLARK, M.A., PH.D.

IN a previous paper[1] I have shown that substituted benzene-1 : 2-dithiols are very delicate and highly specific reagents for tin, and that after addition of thioglycollic acid the test is independent of the initial state of oxidation of the metal. Details have also been given of a method by means of which tin can be roughly estimated with 4-chlorobenzene-1 : 2-dithiol.

The comparative difficulty associated with the preparation of the 4-chloro-compound, together with the fact that toluene-3 : 4-dithiol is now available commercially ("dithiol"), indicated the necessity for using the latter compound whenever possible. Accordingly a technique has now been worked out by means of which accurate colorimetric determinations of tin may be made with this derivative.

THE REAGENT.—"Dithiol" (0·2 g.) is dissolved in 100 ml. of 1 per cent. sodium hydroxide solution, and 0·3 to 0·5 g. of thioglycollic acid is added. The reagent thus prepared is stable for a considerable time, and there is no need to keep the solution in an atmosphere of hydrogen. If at any time a milky white suspension of the disulphide is formed, the reagent should be discarded.

METHOD.—If a solution containing tin is heated after addition of the "dithiol" reagent, the red precipitate rapidly coagulates and accurate colorimetric work is rendered impossible. Coagulation can, however, be stopped by the addition of agar-agar, as suggested by Dr. T. P. Hoar.

For the determination of tin the acid solution containing the metal is treated with thioglycollic acid (a few drops per litre) to ensure reduction to the stannous state and is then diluted until it contains not more than 60 p.p.m. of tin. A measured quantity (5 ml.) of this solution is placed in a graduated test-tube, and 1 ml. of conc. hydrochloric acid and 1 ml. of a warm jelly of agar-agar are added. The solution is then carefully heated to boiling and maintained at that temperature

for a few seconds until the whole of the agar-agar is in solution. It is immaterial whether the tin-containing solution is added before or after the boiling of the solution, but unless the agar is completely dissolved the final colour fluctuates and reproducible results cannot be obtained. The tube is then cooled under the tap, and 2 ml. of the reagent, together with sufficient water to bring the total volume to 10 ml., are added. Finally, the tube is immersed in a boiling water-bath for 60 seconds, after which the liquid is ready for colour measurement.

Measurement of the Colour.—Attempts to measure the colour by transmitted light showed that matching was difficult, the red colour being associated with a large proportion of yellow. As in the previous work, satisfactory results were obtained by the use of reflected light.

For this purpose a Lovibond tintometer, British Drug Houses pattern, was tipped up on its back edge, so that the tray lay in a horizontal plane, as shown in Fig. 1. A standard porcelain tray (3·3 × 3·3 cm.) was placed in position, and 2·0 ml. of the hot liquid were at once removed from the test-tube (which had previously been taken from the water-bath), by means of a calibrated dropping pipette and placed in the tray, giving a depth of liquid of almost exactly 2·0 mm. after cooling. The colour was then matched against the standard tinted slides.

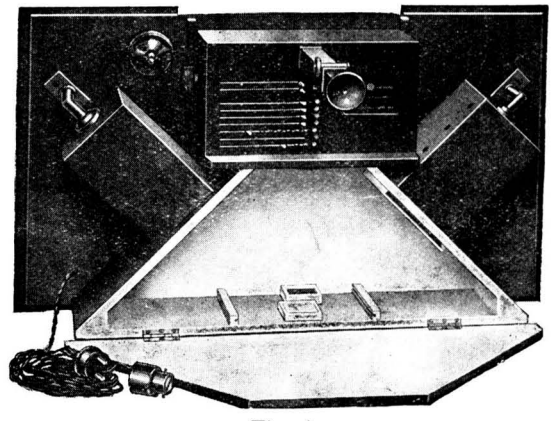

Fig. 1

For purposes of measurement the red units only were considered as significant, although it was always necessary to introduce a small amount of yellow into the matching colour, and occasionally a neutral tint, to adjust the brightness. It was found that the colour did not alter by more than 0·1 unit on standing for ten minutes, provided that the agar-agar was properly dissolved. Whenever alterations greater than this occurred, the results were ignored. In every instance the measurements could be repeated to within 0·2 red unit, and nearly always within 0·1 red unit over the range of concentrations of tin examined, that is to say, the accuracy of colour measurement was not less than that with which other variables were reproduced.

The figures obtained for a series of tin solutions of various concentrations are reproduced on p. 663, and in Fig. 2 the red units have been plotted against the

tin-content in parts per million. It will be seen that a smooth curve is obtained for concentrations of tin up to 30 p.p.m. Beyond this point, however, irregularities occur, although it was found that individual readings were always repeatable. From these results it appears that, for measurements of the highest attainable accuracy, a tin concentration above 30 p.p.m. is inadvisable.

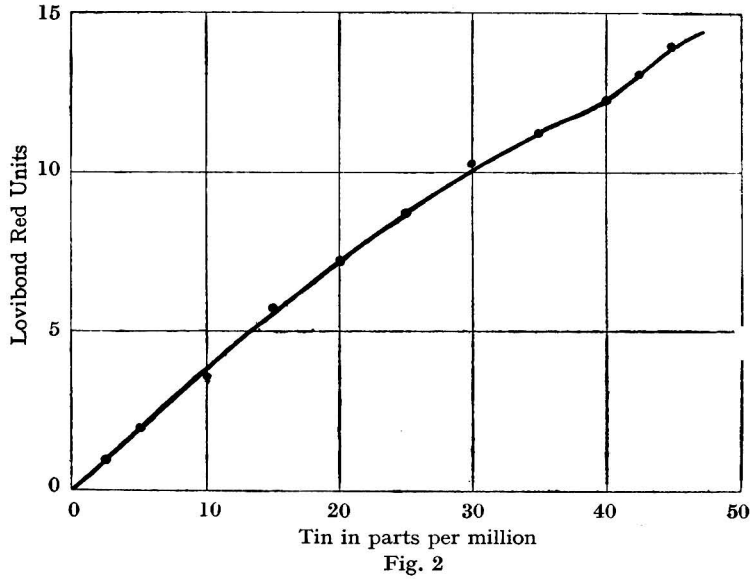

Fig. 2

Tin p.p.m. after dilution to 10 ml.	Colour (five minutes after removal from water-bath)		
	Red units	Yellow units*	Brightness* (Neutral units)
2·5	1·0	0·4	0
5	2·0	0·7	0
10	3·6	0·9	0·1
15	5·7	0·9	0
20	7·2	0·7	0
25	8·7	1·2	0·1
30	10·2	0·9	0·1
35	11·2	0·6	0·1
40	12·3	1·0	0
42·5	13·1	0·9	0·1
45	14·0	1·0	0
50	14·9	1·0	0·2

* Considerable variations were sometimes observed.

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Notes

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

THE OCCURRENCE OF COPPER IN PRESERVED PEEL (CITRON, ORANGE AND LEMON) AND IN GLACÉ CHERRIES

DURING the past few months I have experienced great difficulty in obtaining samples of the above-mentioned products (sugared or syruped) entirely free from copper. The amounts varied from 10 to 28 parts per million. Although, as a rule, the contamination is apparently due to the use of copper utensils during the manufacturing process, the matter is of importance, in view of the fact that copper colouring matter is prohibited by the Public Health (Preservatives, Etc., in Food) Regulations, 1925. Most of the determinations were made colorimetrically by several different methods, but in every instance both the dithio-oxamide and the sodium diethyldithiocarbamate reagents were used, the sample being prepared by the usual wet oxidation process with nitric and sulphuric acids.

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TITRATION OF CARBONATES

WHEN carbonate is titrated with a dilute acid the indicator gives the "acid" colour, and after a brief pause returns to the "alkaline" colour; this occurs when the bicarbonate stage has been reached and continues until all the carbonate is in the form of hydrogen carbonate, when the indicator remains permanently at the "acid" colour. This phenomenon was first noted by Thiel, who published papers in the *Berichte* in 1913 (see also McBain, *J. Chem. Soc.*, 1912, p. 814, and Beckurt's *Die Methoden der Massanalyse*, 1931, p. 247); it is ascribed to the time taken to reach equilibrium $CO_2 + H_2O \rightleftharpoons H_2CO_3$.

It has been found here that the phenomenon is also well shown by the newer indicators, such as bromocresol purple and bromothymol blue, the colour change of which takes place between *p*H 5 and *p*H 8. On adding single drops of $N/10$ acid to $N/100$ sodium carbonate solution the period of delay is two or three seconds; on adding $N/10$ sodium hydroxide solution to $N/100$ carbonic acid solution the delay is longer—up to 15 or 20 seconds. Analogous results have been noted with dilute sulphurous acid and dilute ammonium hydroxide.

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MONKTON COMBE SCHOOL
NEAR BATH

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 AND COUNTY OF BRISTOL

REPORT OF THE PUBLIC ANALYST FOR 1936

OF the 1662 samples of food and drugs examined, 598 were formal and 1064 informal.

"MILK-O."—A sample sold under this fancy name gave the following analytical figures: Sp.gr., 1032·8; fat, 0·50; non-fatty solids, 8·55; ash, 0·65; chlorine in ash, 14·5 per cent.; Δ, 0·456°; starch present. It was probably made by boiling skimmed milk powder and starch with water. The cipher after the word "milk" is not supposed to be a measure of its value, but rather a ruse so that it does not come under the Sale of Milk Regulations, 1901 and 1912.

GROUND ALMONDS AND CASHEW NUTS.—The following results were obtained in the analysis of 9 samples of genuine ground almonds and 1 of ground cashew nuts, which are said to be a good and cheap substitute for ground almonds:

	Moisture Per Cent.	Ash Per Cent.	Oil Per Cent.	n_D^{40} of oil	Iodine value of oil
Ground almonds (mean of 9)	3·5	2·84	59·4	1·4632	96·3
Ground cashew nuts	3·7	2·55	30·0	1·4624	86·0

Two samples of ground almonds were adulterated with 10 and 4 per cent. of brown sugar, respectively.

MERCURIAL OINTMENT.—Five of 8 samples of weak mercury ointment contained about 10 per cent. of mercury, as required by the B.P. Codex, 1934; one contained about 15 per cent., and two were deficient in mercury (8·65 and 8·5 per cent.). One of these deficient samples, which had been purchased in a glazed cardboard box, was examined again after being 5 months in the laboratory, and was then found to contain 10·65 per cent. of mercury. Tests were therefore made with three samples of a mercurial ointment kept in different containers, and the following amounts of mercury were found:

Nature of container	Glazed cardboard Per Cent.	Wood-chip Per Cent.	China pot Per Cent.
Analysis made—			
1 day after purchase ..	9·7	9·6	9·6
3 weeks after purchase ..	11·1	10·1	9·6
5½ months after purchase ..	12·75	10·7	9·8

Thus it is useless to expect a correct determination of the mercury in an ointment of this type sold to the purchaser in a glazed cardboard box, unless the analysis is made within a day or two after the purchase.

AMMONIA IN SHRIMPS.—A tinned sample of shelled shrimps was examined, owing to exception having been taken by another authority to the presence of ammonia. The sample yielded 0·033 per cent. of ammonia on distillation with magnesium oxide, but it was not abnormal in this respect, since shelled fresh shrimps yielded 0·055 per cent. under the same conditions.

FEATHERS AND UPHOLSTERY MATERIAL.—It is said that imported feathers are usually cleansed, but that home-produced feathers are often sold unwashed (*cf.* ANALYST, 1928, **53**, 278; 1936, **61**, 252, 473). Tests were applied to 7 samples of feathers of unknown origin as follows:—Fifty g. were shaken at frequent intervals for 30 minutes in a large stoppered bottle with 1·5 litre of cold distilled water, the mixture was strained through a Buchner funnel, and the feathers were wrung out by pressure. The resulting effluent was filtered twice, and the soluble chlorine in the filtrate was determined gravimetrically. The oxygen absorbed in 4 hours from $N/80$ potassium permanganate solution at 27° C. was also determined.

In washing experiments, the original feathers were shaken for an hour with 3 litres of tap water, and the feathers were then wrung out by pressure and left for about a week on the floor of a sunny room. The moisture-content of the feathers before and after washing ranged from about 8 to 9 per cent. The effluent from the washed feathers was made in exactly the same way as the original effluent. Subsequently it was found that substantially the same chlorine figure was obtained by washing the 50 g. of feathers used for obtaining the original effluent, with 1·5 litre of cold tap water for an hour, wringing out with pressure, and filtering twice. The results obtained with the feathers and with various upholstery materials were as follows:

	Chlorine Parts per 100,000				Oxygen absorbed in 4 hrs. at 27° C. Parts per 100,000			
	Original effluent	After washing 1st	2nd	3rd	Original effluent	After washing 1st	2nd	3rd
Mixed featherdown ..	175	27	5	3	94	39	18	13
Poultry feathers ..	188	26	5	4	80	31	12	9
Duck feathers	160	39	13	—	47	34	12	—
Poultry feathers ..	15	13	—	—	30	26	—	—
Mixed poultry chopped feathers ..	45	16	—	—	90	42	—	—
Cheap mixed feathers ..	77	19	—	—	124	44	—	—
Duck feathers ..	145	47	20	—	150	46	20	—
Hair (new black) ..	8	—	—	—	13	—	—	—
Blackfield hair	18	—	—	—	19	—	—	—
Kapok	15	—	—	—	290	—	—	—
,, ...	56	—	—	—	489	—	—	—
Curled coconut fibre ..	56	—	—	—	111	—	—	—
New cotton waste ..	87	18	6	—	646	146	32	—
Millpuff	102	14	7	—	873	146	49	—
,, (white mixture)	27	—	—	—	541	—	—	—
,, (dark mixture)	40	—	—	—	258	—	—	—
Rag flock	35	10	6	—	202	61	28	—

These experiments show that it is quite practicable to wash feathers to conform with the standard of cleanliness prescribed for rag flock. F. E. NEEDS

METROPOLITAN BOROUGH OF HAMMERSMITH

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1936

"DAIRY TABLE CREAM."—A sample sold under this name was found to consist of chocolate-flavoured blanc-mange powder, and contained no cream or milk powder; it was reported as adulterated.

WHITE MILK CHOCOLATE.—This was found to have been prepared from cocoa butter with milk and sugar (probably added as sweetened condensed milk), with no non-fatty cocoa solids. Cocoa butter is somewhat difficult to digest, and my information is that this so-called chocolate has not proved a success owing to its having caused biliousness in children. It was reported as adulterated.

F. W. EDWARDS

CITY OF SALFORD

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1936

MEASUREMENT OF SOLAR RADIATION.—*The Potassium Iodide Method.*—This process has been in continuous use for ten years. Although it suffers from several disadvantages (*cf.* ANALYST, 1927, **52**, 641; 1929, **54**, 101, 334; 1931, **56**, 314), the results are very consistent under standardised conditions. The figures for July, 1936, show a sudden drop, with a corresponding rise in August; this is almost certainly due to the heavy rainfall and resulting cloudy conditions in July.

The Nitrite Method.—This has been developed from the original work of Gillam and Morton (*J. Soc. Chem. Ind.*, 1927, **46**, 415; Abst., ANALYST, 1928, **53**, 60), who found that nitrite is developed by the action of ultra-violet light in an alkaline solution of potassium nitrate. In the modification adopted at Salford two parts of the same solution of alkaline nitrate are exposed side by side, one in a quartz tube and the other in a glass tube, and the difference in the amounts of nitrite formed is measured either by the Griess–Ilosvay method or the Riegler method. Although this nitrite can be formed only by ultra-violet light of wave-length below approximately 320$m\mu$,* the curve of the results obtained shows a striking resemblance to that of the curve of the results obtained by the potassium iodide method; this would seem to indicate that the ultra-violet rays below 320$m\mu$ vary in direct proportion to the total amount of solar radiation received.

Ashworth's Ultra-Violet Ray Meter.—The first type of this instrument (ANALYST, 1933, **58**, 690) has been superseded by one in which the paper wedge is replaced by varying thicknesses of wire gauze; this prevents any variation in the transmission factor due to dampness or to the discoloration of the wedge by sunlight. The transmission of the glass filter used is between 300 and 400$m\mu$, with a maximum transmission of 80 per cent. at 360$m\mu$. The wave-length of the rays of greatest medicinal value is of the order of 300$m\mu$.

In my opinion, whilst the instrument will give definite information as to the total ultra-violet rays in solar radiation, yet, having regard to our knowledge of the extremely small amounts of ultra-violet rays of wave-length 300$m\mu$ present, especially in winter sunshine, it cannot be assumed that a positive reading for ultra-violet rays with this instrument also indicates the presence of rays of therapeutic value.

The following table shows the relative intensities of ultra-violet light recorded at Salford and by a similar instrument at the Meteorological station at Southport:

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Regent Road, Salford	3·4	2·6	21	20	61	89	68	66	32	18	8	11
Hesketh Park, Southport	—	—	52	85	115	245	183	92	47	25	11	10

Integrating Solarimeter.—An instrument of this type, which is essentially a Moll pattern thermopile coupled with a sensitive milliampere-hour-indicator, was installed during the early part of the year. In this apparatus, which is calibrated

* Ordinary glass bottles will transmit all rays longer than 320$m\mu$; quartz transmits rays down to about 200$m\mu$. Ultra-violet light from the sun is normally 300–400$m\mu$.

by being exposed to a standard source of radiation, the solar radiation is transformed into, and recorded as electrical energy. The results are thus in terms of absolute units of energy and have a distinct advantage over those obtained by the other methods. The thermopile is non-selective and records total solar radiation, both visible and invisible. So far as I am aware, the only other instrument of this type in use is a recording solarimeter recently installed at the Meteorological Office, South Kensington. The following table gives the comparative figures, expressed in gram calories per sq. cm., for three months, obtained by the two instruments:

	Salford	South Kensington
September ..	99	188
October ..	53	110
November ..	12	42

ATMOSPHERIC SULPHUR POLLUTION.—Twenty-four monthly tests were made by the lead peroxide method (ANALYST, **1935**, **60**, 122) and 253 tests at Regent Road by the volumetric sulphur method. In the former process sulphur pollution is returned as mg. of SO_3 per 100 sq. cm. of exposed surface, and in the latter the sulphur dioxide in the air is expressed as parts per million. Both processes show a very striking rise during the winter months, and the volumetric process (which enables daily determinations to be made) also shows very high results during foggy weather. The daily averages of sulphur dioxide in p.p.m. were as follows:

Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
0·070	0·094	0·075	0·073	0·073	0·047	0·042	0·039	0·037	0·033	0·093	0·071

G. H. WALKER

Department of Scientific and Industrial Research

WOOD PRESERVATIVES*

THE Report discusses the advantages and disadvantages of the various types of preservatives.

A. OIL TYPE PRESERVATIVES.—*Coal-tar Creosote.*—A brief account of the production and properties of various creosotes has been given by Richardson (*J. Brit. Wood Pres. Ass.*, 1934, **4**, 64). The British Standard Specification No. **144**—1936 covers practically all the creosotes produced in this country and includes standard methods of test. Owing to the false idea that a good creosote must be black, it is difficult in practice to obtain creosoted wood of a light colour; black creosotes are invariably dirty.

Coal-tar.—This is less efficient as a preservative than the creosote derived from it, partly because it does not penetrate the wood so deeply. In admixture with creosote it is a satisfactory preservative for pressure treatment, but there is a tendency for the surface of the wood to be covered with a pitch coating which does not dry off.

Water-gas Tar Creosote.—Water-gas tar and its distillates have little or no toxicity for wood-destroying fungi, and their use should therefore be limited to diluting coal-tar creosotes. The distillates, sometimes offered as creosotes, are usually brown and are characterised by the lack of tar acids, a minimum content of which is demanded in all specifications for genuine coal-tar creosote.

Wood-tar Creosote.—Creosotes produced by the distillation of wood-tar are not prepared to any standard quality, and cannot compete in price with ordinary

* *Forest Products Research Records*, No. 17 (*Wood Preservation Series*, No. 3). By N. A. Richardson, B.Sc., A.I.C. H.M. Stationery Office, 1937. Price 6d. net.

coal-tar creosote. They are good preservatives, but are said to be more corrosive than ordinary creosotes to metals. They are sometimes added to proprietary preservatives of coal-tar origin, particularly those intended to give the wood a warm, brown colour.

Petroleum Oils.—In U.S.A. and India crude petroleum, "topped" petroleum and petroleum fuel oils are used in admixture with coal-tar creosote, particularly for the preservation of railway sleepers. In themselves they have little, if any, toxicity for wood-destroying fungi.

Waste Sump Oil.—Used by itself waste sump or crank-case oil is practically non-toxic to wood-destroying fungi, although it might be used as a solvent for an oil-soluble toxic material. Tetrachlorophenol has been suggested as a suitable chemical to dissolve in the oil.

B. WATER-SOLUBLE TYPE PRESERVATIVES.—Recent developments in this type of preservative have aimed at producing water-insoluble compounds in the wood from mixtures that are water-soluble at the time of treatment.

Zinc Chloride.—The best results are obtained by an impregnation treatment, such as a pressure process. A common strength for the solution is 3 to 5 per cent.; at high concentrations the wood substance is attacked, and it is therefore not advisable to use solutions stronger than 5 per cent. Zinc chloride solutions are slightly more corrosive than creosote solutions to iron and steel.

Sodium Fluoride.—This is the basis of several proprietary preservatives of Continental origin. Solutions of 2 to 4 per cent. in soft water are commonly used; a 4 per cent. solution is practically saturated at ordinary temperatures.

Magnesium Silicofluoride.—The salts of hydrofluosilicic acid are toxic to wood-destroying fungi; the magnesium salt is the one generally used, owing to the relative insolubility of the others. It should not be used in contact with metal or glass.

Copper Sulphate.—Although toxic to wood-destroying fungi, copper sulphate has the disadvantage of low permanency on account of its high solubility. It is not much used in this country, probably because its action upon iron prevents it being used in ordinary treating plants.

Mercuric Chloride.—This salt formed the basis of the Kyanising process. Its extreme toxicity to human beings and animals and its corrosive action account for its not having been used to any extent in this country.

Arsenic.—Arsenic in various forms has been a common ingredient of preservatives for protecting timber against the attack of white ants. It is unlikely to be used much in this country because of its poisonous character.

Recent Developments in Water-soluble Preservatives.—The use of zinc meta-arsenite (Z.M.A.) has been suggested by Curtin. Although insoluble in water, it is soluble in dilute acids, so that by using an acetic acid solution of the salt, the preservative is slowly deposited in the wood as the acid evaporates.

It has been found that alkali dichromates are able to fix certain salts in wood, and wood preservative salt mixtures containing alkali chromates have therefore been patented.

C. SOLVENT TYPE PRESERVATIVES.—On the whole these preservatives, especially those containing solvent naphtha, penetrate the wood somewhat better than the other types, and are thus more suitable for methods of spraying or brushing the timber. A drawback is that they are relatively more expensive than the other types.

Toxic chemicals used include metallic salts or metallic (especially copper and zinc) salts of organic acids such as naphthenic, abietic and oleic acids, phenols such as β-naphthol, chlorinated phenols and hydrocarbons such as chlorinated naphthalene.

PATENTED AND PROPRIETARY PRESERVATIVES.—Frequently extravagant claims are made for these preservatives without due regard to the comparatively

small protection afforded the timber by the slight penetration resulting from a surface application. All the types previously mentioned are represented in this class of preservatives, but so far as this country is concerned the oil type predominates. Many of that type are derived from coal- or wood-tar or mixtures of these, and are generally refined to produce oils that are cleaner and more penetrating than ordinary creosote. Frequently, certain substances are taken out of the distillates to ensure that they are fluid at ordinary temperatures and to increase their penetrating properties. Sometimes pigments or dyes are added to give a decorative value. Speaking generally, the preservatives manufactured by reputable firms are efficient and can be safely used.

Conference on Atmospheric Pollution

ON June 1st thirty-eight representatives of local authorities and other organisations co-operating with the Department of Scientific and Industrial Research met at the offices of the Department in the half-yearly conference. The gathering included representatives from Barnsley, Birmingham, Dagenham, Glasgow, Halifax, Hull, Leicester, Liverpool, London, Manchester, Newcastle, Rotherham, Salford, Scarborough, Sheffield, Stoke-on-Trent, Walsall, Westminster, Willesden, Wolverhampton, The British Electrical Development Association, The British Commercial Gas Association, Messrs. Cadbury Bros. and The Thames Nautical Training College.

In the absence, owing to indisposition, of the Chairman (Mr. W. Brownhill Smith, M.V.O., D.L.), Dr. H. A. Des Voeux, a past Chairman, presided.

Dr. G. M. B. Dobson, F.R.S., Chairman of the Atmospheric Pollution Research Committee, presented the usual report on the progress of the investigations carried out under the Committee. The Conference noted in particular that systematic observations in connection with the intensive survey of the pollution in and around the City of Leicester were begun on April 1st. During the preceding four months the Survey staff were occupied in installing different standard measuring apparatus at twelve sites and in certain trial routine observations. The Conference were very appreciative of the generous help afforded by the authorities at Leicester in starting the work. The decision of the authorities to equip and maintain a station for regular meteorological observations was greatly welcomed.

The Conference also recorded their appreciation of the valuable assistance given by the Public Analysts of Glasgow, Hull and Sheffield, in an investigation of the possibility of combining a dust filter with apparatus for the volumetric determination of sulphur dioxide in the atmosphere. This was regarded as an excellent illustration of the value of the collaboration of co-operating bodies with the Research Committee in work of this kind.

The Conference were glad to receive a report submitted through the Medical Officer of Health for Leeds on the analysis of dust samples collected in Leeds, Halifax and Huddersfield.

The Conference endorsed a proposal of the Research Committee that a meeting of Public Analysts and others who are directly responsible for making observations on behalf of co-operating bodies should be convened to discuss technical problems and to interchange ideas on the measurement of atmospheric pollution.

Mr. Brownhill Smith retired from the Chairmanship of the Conference, having served for three consecutive years, the maximum period permitted by the Rules and Standing Orders. Alderman David Adams, M.P., J.P., a representative of Newcastle-upon-Tyne, was elected Chairman for the ensuing year.

Trinidad and Tobago

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1936

IN his Annual Report, Mr. H. S. Shrewsbury states that 4376 samples were examined for various Government Departments, and 117 for private firms and persons. As there are no consulting analysts in local practice, private samples may be examined on payment of a fee, but such work is of secondary consideration to Government work. Of the 1055 samples examined under the Food and Drugs Ordinance, 277 were of milk, 316 of aerated waters, 143 of coffee and 124 of butter.

ADULTERATION OF COFFEE.—It was not until 1932 that coffee was found to be adulterated in Trinidad (*cf.* ANALYST, 1933, **58**, 696). In 1936 eight of the 143 samples examined were adulterated. In 1935 the adulterant was burnt sugar, whilst in 1936 burnt sugar and starchy materials were used.

FRIOLENE OILS.—Eighty-two samples of Friolene and Buttercup oils (derived from coconut oil) were examined; two were adulterated with olive oil, which is more expensive.

Food Poisoning: Its Epidemiology and Bacteriology*

AT the Ministry of Health 58 outbreaks of food poisoning were recorded in 1934 and 129 in 1935. They are discussed under three headings: (1) those due to the multiplication, within the body, of pathogenic bacteria present in food—the "infection" type; (2) those due to the ingestion of certain substances formed as the result of bacterial multiplication in the food before ingestion—the toxin type; (3) those due to the toxin of *Clostridium botulinum*—botulism.

(1) *The "Infection" Type.*—Among the organisms responsible for this type, members of the *Salmonella* group are the most common (*cf.* Savage and Bruce White, ANALYST, 1925, **50**, 341), but members of the Dysentery group (Sonne and Flexner) must be included. In 1935 the former were responsible for 53 and the latter for 12 outbreaks, 8 being attributable to the Sonne bacillus, and in 1936 an outbreak due to *B. proteus* (*cf.* ANALYST, 1925, **50**, 556) was recorded by Gray. From antigenic analysis it is justifiable to place typhoid and paratyphoid bacilli in the *Salmonella* group, but generally, and almost invariably, the symptomatology and epidemiology of typhoid and paratyphoid infections are very different from those of the food-poisoning bacilli. A few instances, however, have been recorded of bacilli of the *Salmonella* group giving rise to symptoms similar to those caused by typhoid and paratyphoid bacilli, *i.e.* continued fever, as opposed to acute gastro-enteritis, and *vice-versa*. The bacillus most commonly responsible for food poisoning outbreaks is *Bact. typhi-murium* (*B. aertrycke*); during the decade 1923–1933 the Ministry of Health found this organism in 110 of 186 outbreaks.

(2) *The "Toxin" Type.*—Notwithstanding exhaustive investigations into many outbreaks, it has not been possible to isolate any toxins produced by members of the food-poisoning or dysentery groups. These outbreaks were formerly

* Paper by E. R. Jones, M.D., D.P.H., F.I.C. (Senior Pathologist, Kent County Council), read at the Congress of the Royal Institute of Public Health and Institute of Hygiene, Margate, 1937; *Brit. Med. J.*, July, 1937, p. 106.

designated as ptomaine poisoning, but the ptomaines or toxic amines are not produced until food reaches an advanced stage of decomposition, and they are relatively non-toxic, except in very large doses. Potent toxins, however, are produced by certain strains of *Staphylococcus albus* and *aureus* under certain conditions; it has been suggested by Savage, with considerable experimental support (*cf.* ANALYST, 1927, **52**, 123), that similar toxins are elaborated by members of the *Salmonella* group, that the bacilli are killed in the cooking, but that the toxins survive and cause food poisoning. Bacteria capable of giving rise to toxic substances under certain conditions are not confined to these two groups, among them may be mentioned *B. coli*, *Proteus vulgaris*, *Proteus Morgani*, *Streptococcus viridans*, and a micrococcus found in milk. The common ways in which food may be infected are as follows:

(*a*) Infected animals may be used for food; for example, meat (beef and pork), ducks or their eggs (*cf.* Scott, ANALYST, 1930, **55**, 595). (*b*) Infected animals (*e.g.* rats, mice and bovines) may excrete specific organisms that contaminate food. (*c*) Human carriers may contaminate the food by handling.

(3) *Botulism.*—The causative organism, *Cl. botulinum*, is a normal inhabitant of the surface layers of soil. It is incapable of growth in the animal body and of giving rise to infection, but under certain conditions it produces a very potent toxin. The spores are very resistant to heat; the potted duck paste in the Loch Maree cases had been heated on three occasions, and at one stage to 115° C. for 2 hours (*cf.* ANALYST, 1923, **48**, 118). The toxin is destroyed by such heat as is ordinarily applied in cooking. In Europe most cases have been caused by preserved meat or meat paste; in America by canned vegetables and occasionally by canned fruits.

D. R. W.

British Standards Institution

BRITISH STANDARD SPECIFICATION FOR PORTABLE CHEMICAL FIRE EXTINGUISHERS: FOAM, AND CARBON TETRACHLORIDE, TYPE

THIS Specification (No. 740—1937) is supplementary to B.S. No. 138 (Portable Chemical Fire Extinguishers, Acid Alkali Type). It has been approved by the Chemical Engineering Industry Committee and endorsed by the Engineering Divisional Council, and is intended to include the technical provisions necessary for the supply of the articles referred to.

(1) The Foam type is one in which the pressure required to eject the liquid contents is generated by the chemical action of a solution of an acid salt stored in an inner receptacle, in conjunction with a carbonate or bicarbonate solution in combination with a stabiliser, stored in the outer container of the extinguisher. A foam is produced by the combination of the "inner" and "outer" solutions.

(2) In the carbon tetrachloride type, carbon tetrachloride is propelled from the extinguisher by means of (*a*) hand force pump mechanism; (*b*) release of compressed carbon dioxide or nitrogen from an attached cylinder; (*c*) pressure of carbon dioxide stored in the carbon tetrachloride container; (*d*) pressure of air from a self-contained air pump.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Diacetyl in Butter. J. Pien, J. Baisse and R. Martin. (*Le Lait*, 1937, **17**, 673–698.)—A new method for the determination of diacetyl in butter is described. The apparatus consists of a 300-ml. flask fitted for steam-distillation and connected with a Liebig condenser by means of a long upright tube having a constriction followed by a bulb near the upper end. The condenser outlet is attached to an adapter which is drawn out to a capillary reaching almost to the bottom of an Esbach tube. The butter (50 to 100 g.) is placed in the flask and 0·5 ml. of water in the Esbach tube. The sample is distilled with steam until 10 ml. of distillate have been collected in the Esbach tube, which is then removed and replaced by a similar tube, and a second 10 ml. is collected. The distillate in each tube is treated with 0·5 ml. of a freshly prepared solution of diaminobenzidine (2·5 per cent.), and the liquids are well mixed. To the mixture 0·5 ml. of conc. hydrochloric acid is added, and the whole is again well mixed. After 2 minutes the colour is compared with that of a standard solution of potassium dichromate which is a dilution of a 1 per cent. solution, but the dilutions are not in linear relationship to the diacetyl with which they correspond, and a table in the original paper should be consulted. The amount of diacetyl present in butter showed no significant variation with the season of the year, nor with the district from which it was obtained, but, as was already known, was dependent on the methods of separating the cream and preparing the butter. During the distillation the flask is not heated directly, and the steam current is so regulated that the rising vapours from the flask have to bubble through condensate in the bulb. Under these conditions all the diacetyl can be obtained in the first 10 ml. of distillate, and the second 10 ml. should contain none. (See also Barnicoat, ANALYST, 1935, **60**, 653.) S. G. S.

Physico-Chemical Investigation Incidental to the Study of Chocolate Fat Bloom. Part I. W. Clayton, S. Back, R. I. Johnson and J. F. Morse. (*J. Soc. Chem. Ind.*, 1937, **56**, 196–199T.)—Oxidised cocoa butter has the property of inhibiting fat bloom in chocolate and the deposition of stearine in chilled olive oil. Air is blown through cocoa butter at 250° C. until the iodine value is about 20, the molecular weight meanwhile increasing from 890 to about 1600. Blown cocoa butter is regarded as of polar character—mainly a polymerisation product of oxidised oleo-disaturated glyceride, the structural unit being probably a dimeride. Confirmation of the polar type of molecular structure was obtained by means of the surface film technique of Langmuir and Adam. The presence of blown cocoa butter slightly depresses the complete fusion point of ordinary cocoa butter and has a marked effect on the solidification, which takes place without the usual formation of clumps of crystals. The blown fat is regarded as exhibiting a definite balance between hydrophylic and hydrophobic molecular groupings which lead

to adsorption-orientation phenomena. To determine the influence of blown cocoa butter and of lecithin on fluidity (1) 0·6 per cent. of the blown fat and (2) 0·6 per cent. of lecithin were added, respectively, to systems of (*a*) cocoa, 135 g., and fat, 40 g.; (*b*) sugar, 160 g., and fat (cocoa butter), 55 g.; (*c*) dry milk powder, 300 g., and fat (cocoa butter), 185 g.; (*d*) moist milk powder and fat (30 ml. of water were added to (*c*)), and the increase of mobility was measured. Percentage increases were:—*a*, (1) 127, (2) 33; *b*, (1) 26, (2) 89; *c*, (1) 280, (2) 520; *d*, (1) 220, (2) 270. Blown cocoa butter is thus superior in the hydrophobic, and lecithin in the hydrophylic systems.

The addition of quantities up to 1 per cent. of blown cocoa butter to normal olive oil, which is then chilled to 2 to 4° C., inhibits the deposition of stearine according to the amount of blown fat and its iodine value. Whilst the control oil set solid in a few hours, the treated oil remained clear and fluid for 4 years (the duration of the experiment). It was found that the capacity of blown cocoa butter to inhibit stearine deposition runs quantitatively parallel with its efficacy in preventing fat bloom in chocolate, and it is suggested that the same physico-chemical cause operates to prevent crystallisation in chilled olive oil and stored chocolate. The formation of bloom in nut-centred chocolates is not completely inhibited by even the best blown cocoa butter (although it is greatly reduced), possibly because there may be interference due to preferential adsorption at the fat crystal—fat interface by the nut oils. D. G. H.

Siene Bean and Oil. T. S. Perrin. (*J. Amer. Chem. Soc.*, 1937, **59**, 1401–1402.)—The Siene bean plant (*Daubentonio longifolia*), sometimes called the "coffee bean" or "rattle box," grows abundantly inland and along the Gulf Coast of Texas and Florida and may attain the size of an average peach tree. The trees are hardy and bear prolifically, the pod containing 4 to 8 seeds, which are extremely toxic to sheep and (in the laboratory) to guinea-pigs. The water-soluble portion of the seeds (17·5 per cent.) formed a foaming soap-like emulsion, and contained 2·3 per cent. of protein calculated on the original sample. The soluble substances gave negative results in tests for sugar and starch, but on hydrolysis the original sample was found to contain 8·6 per cent. of sugar (calculated as dextrose). The seeds contained:—Moisture, 11·7; fat, 3·8; starch, 27·9; protein, 21·2; fibre, 17·7; ash, 2·8; non-protein water-soluble matter, 15·2 per cent. The crude oil, as extracted with ether, had: sp.gr. at 25/25° C., 0·9209; n_D^{25}, 1·4730; saponification value, 194·2; iodine value (Hanus), 97·3; acetyl value, 6·9; acid value, 4·5; unsaponifiable matter, 3·0 per cent.; it contained 13·8 per cent. of saturated acids and 78·4 per cent. of unsaturated acids (iodine value, 120·6). D. G. H.

New Purine in Tea. T. B. Johnson (*J. Amer. Chem. Soc.*, 1937, **59**, 1261–1264.)—Concentrated tea residues from the commercial removal of caffeine were treated with warm methanol, and the extract, when filtered and cooled, deposited hexagonal crystals, which were picked out mechanically and purified by crystallisation from boiling water. The substance, which was characterised by its crystalline structure, sharp m.p. (225° C.) and neutral reaction, was identified as 1, 3, 7, 9-tetramethyl-2, 6, 8-trioxypurine. It is, in fact, the first methylated derivative of 2, 6, 8-trioxypurine (uric acid) to be discovered in nature. This

purine (tetramethyl uric acid) was first synthesised by Emil Fischer (*Ber.*, 1884, **17**, 330, 1784), and was afterwards described by Reuter (*Ber.*, 1897, **30**, 3009). The crystallographic characteristics of the present material, isolated from tea, agree exactly with those in Reuter's description. D. G. H.

Biochemical

Simple Method for the Determination of Acetone in Blood and Urine. J. C. Abels. (*J. Biol. Chem.*, 1937, **119**, 663–667.)—The apparatus consists of a 50-ml. Erlenmeyer flask having a tightly fitting cork. Suspended from the under surface of the cork by means of a pin is a 1-cm. length of cotton pencil, which is a compressed roll of cotton used by dentists. The urine is made acid to Congo red with a 1:1 solution of sulphuric acid, and 0·5 ml. is pipetted on to the cotton roll. With blood no previous acidification is necessary, and 0·5 ml. of the sample may be used directly. Over the bottom of the flask 0·5 ml. of a 5 per cent. solution of sodium bisulphite is spread, and the cork is carefully and firmly inserted, so that the blood or urine sample is suspended about 1 cm. above the level of the bisulphite. The flask is heated in a boiling water-bath for 15 minutes and, after cooling, the cork and cotton roll are removed. One ml. of water is added, then 1 ml. of Nessler's reagent, bringing the total volume to 2·5 ml. The liquid is poured into a test-tube (6 in. × 0·5 in.), and the turbidity is compared with standards. These standards are prepared at the same time in similar test-tubes from 0·002, 0·004 . . . . 0·010 mg. of acetone, water to 1 ml., 0·5 ml. of 5 per cent. sodium bisulphite solution and 1 ml. of Nessler's reagent. The full development of the turbidity requires 15 minutes. Standards will keep for 24 hours if exposed to light as little as possible. The amounts of acetone in blood ranged from 0·3 to 2·0 mg. per 100 ml., and in urine from 0·2 to 2·5 mg. per 100 ml. Recovery of added acetone was from 90 to 110 per cent. S. G. S.

Titrimetric Method for the Quantitative Determination of Lead in Biological Materials. M. K. Horwitt and G. R. Cowgill. (*J. Biol. Chem.*, 1937, **119**, 553–564.)—The lead is extracted from aqueous solution by means of dithizone in chloroform and the extract is freed from excess of dithizone by shaking with aqueous cyanide solution. The lead dithizone complex in the chloroform is then decomposed by shaking with aqueous acid, which removes the lead and leaves in the chloroform the equivalent amount of dithizone. This is titrated with standard lead solution as follows:—The solution of dithizone in chloroform is mixed with dilute cyanide solution, which removes most of the dithizone from the chloroform, imparting a brown colour to the aqueous layer. A lead solution is added from a burette to this mixture until all the dithizone has been re-converted into lead dithizonate, as indicated by the disappearance of the brown colour in the aqueous layer and the absence of a red colour when the aqueous layer is mixed with chloroform and additional lead solution. The dithizone reagent is prepared by dissolving 40 mg. of diphenylthiocarbazone in 400 ml. of chloroform and filtering the solution into a 500-ml. separating funnel. To this are added 50 ml.

of water containing 2 ml. of 25 per cent. hydroxylamine solution, and the whole is shaken. The funnel is kept in a cool dark place, and the chloroform solution is withdrawn as required. The potassium cyanide solution is 0·5 per cent. and is prepared from a 10 per cent. solution which is itself prepared fresh each day. It is essential that the dilute cyanide solution shall be lead-free, and this is ensured by extracting it with chloroform containing dithizone. A stock solution of lead nitrate containing 10 mg. of lead per ml. is also required (1·599 g. of lead nitrate per 100 ml.), and from this a dilute solution containing 0·01 mg. of lead per ml. is prepared. A 20 per cent. solution of sodium citrate is also required, and 800 ml. of this are treated with 8 ml. of 10 per cent. potassium cyanide and extracted with 15-ml. portions of the dithizone solution until free from lead. The citrate mixture is then washed with 25-ml. portions of chloroform and acidified with 4 ml. of 20 per cent. hydrochloric acid, and the extraction of the excess of dithizone is completed with 20-ml. portions of chloroform.

For the determination of lead in blood, 10 ml. of the sample are dried in a 50-ml. silica dish, and the residue is charred. It is then heated in a muffle furnace at about 475° C. for 2 hours, after which the dish is removed. The ash is moistened with 2 ml. of re-distilled nitric acid and warmed until the excess of acid has been driven off, and the dish is returned to the muffle for about half-an-hour. The dish is then placed on a hot-plate, 15 ml. of 20 per cent. hydrochloric acid solution are added carefully, and the whole is heated until the ash is dissolved. The solution is washed into a 125-ml. separating funnel with about 20 ml. of hot water. Ten ml. of 20 per cent. sodium citrate solution and 3 ml. of strong (re-distilled) ammonium hydroxide solution are added to the silica dish, and the contents are well mixed and transferred to the separating funnel with sufficient water to give a total volume of about 75 ml. The contents of the funnel are cooled, 1 ml. of a 25 per cent. solution of hydroxylamine hydrochloride and 1 drop of phenol red solution are added and the whole brought to *p*H 8·0 by the addition of ammonium hydroxide from a burette. The solution is again cooled and to it is added, drop by drop with shaking, 0·5 ml. of 10 per cent. potassium cyanide solution. The mixture is immediately extracted with 0·5 ml. of the dithizone solution and 4 ml. of chloroform. If, after shaking, the chloroform layer does not contain a noticeable excess of dithizone (green colour), further 0·2 ml.-portions are added, and the funnel is shaken, until an excess is present. The chloroform phase is removed to another separating funnel and the aqueous phase is extracted twice more with 0·2-ml. portions of dithizone solution and 2-ml. portions of chloroform. To the combined chloroform solutions 0·5 per cent. potassium cyanide solution is added in such quantity that the volume of the cyanide solution is 1·5 times the volume of the chloroform, and the whole is shaken for 10 seconds. The chloroform layer is transferred to another separating funnel, and the cyanide solution is extracted with 1 ml. of chloroform to recover any traces of lead complex in it. The combined chloroform extracts are again extracted with 1·5 times their volume of 0·5 per cent. cyanide solution, and any lead taken up in this is recovered by extraction with 2 ml. of chloroform. The lead is removed from the red dithizone complex by shaking the combined chloroform extracts for 15 seconds with 2 volumes of 0·5 per cent. hydrochloric acid. The green chloroform layer is withdrawn, and the

acid aqueous solution is again shaken with 1 ml. of chloroform. The chloroform extracts are combined. This chloroform solution of dithizone is then treated with 0·5 volume of 0·5 per cent. cyanide solution and shaken. Most of the dithizone goes into the aqueous layer, giving it a brown colour. Dilute standard lead solution is added from a burette, drop by drop, with shaking after each addition, until only a faint colour remains in the aqueous phase. The red chloroform phase is discarded, and the aqueous layer is washed with chloroform, 2 ml. at a time, until, after shaking, the chloroform layer remains colourless. A drop or two of the lead solution is added, and the whole is shaken for 5 seconds. The pink chloroform solution is withdrawn, and the aqueous layer again extracted with 2 ml. of chloroform, plus a drop or two of the lead solution, until the further addition of lead no longer imparts a pink colour to the chloroform after shaking.

To determine lead in urine, 200 ml. are ashed in a 250-ml. silica dish, as described above, but 5 ml. of nitric acid are used. The ash is moistened with 15 ml. of 20 per cent. hydrochloric acid and heated until almost dry. It is then transferred to a 500-ml. separating funnel with the aid of 15 ml. of the hydrochloric acid, 50 ml. of the sodium citrate solution and 5 ml. of ammonium hydroxide solution. The volume is made up to 250 ml. and, after being cooled and treated with one drop of phenol red solution, the reaction is adjusted to *p*H 8·0, as described. Three ml. of 10 per cent. potassium cyanide solution are now added, and the liquid is extracted with an excess of dithizone, 0·5-ml. portions and 3 ml. of chloroform being used. The procedure is then as described above.

The lead-content of bone is determined by heating the dried bone for 2 hours in a silica dish in the muffle at 475° C. The dish is removed, an amount of nitric acid equivalent to 3 ml. for each 1·5 g. of bone is added, and the mixture is carefully evaporated to dryness. The dish is heated in the muffle for a further half-hour. The contents of the dish are then dissolved in 20 per cent. hydrochloric acid, 15 ml. for each 1·5 g. of dried bone taken, and an aliquot part equivalent to not more than 1·5 g. of dried bone is transferred to a 500-ml. separating funnel. To this are added 75 ml. of the sodium citrate solution, 2 drops of phenol red solution, and sufficient water to give a volume of 350 ml., and ammonium hydroxide is then carefully added, with shaking and cooling, to give a *p*H of 8·0. Five ml. of 10 per cent. cyanide solution are added slowly, and the mixture is extracted with *excess* of dithizone. Three ml. of dithizone solution and 3 ml. of chloroform are added, and the whole is shaken for 30 seconds. If the chloroform layer is not purple, more dithizone—1 ml. at a time—is added until a purple colour persists. The chloroform layer is transferred to a 125-ml. separating funnel, and the aqueous layer is extracted three times, first with 1 ml. of dithizone solution plus 2 ml. of chloroform, then with 0·5 ml. of dithizone plus 2 ml. of chloroform, and finally with 3 ml. of chloroform. The chloroform extracts are combined and extracted once with twice their volume and twice with an equal volume of 0·5 per cent. potassium cyanide solution. The lead is removed from the dithizone complex by washing with 2 parts by volume of 0·5 per cent. hydrochloric acid, and the titration is carried out as described for blood.

All the glassware (including burettes) should be of Pyrex and a blank determination should be made for each type of material. Recovery of lead added to the

various materials in quantities of 0·001 to 0·15 mg. ranged from 90 to 100 per cent. Beef blood (without addition of lead) contained 0·00016 mg. per ml., human urine 0·00003 mg. per ml., and bone ash 0·0085 mg. per g. S. G. S.

Metabolism of Organic Acids of Tobacco Leaf during Culture. G. W. Pucher, A. J. Wakeman and H. B. Vickery. (*J. Biol. Chem.*, 1937, **119**, 523–534.)—The three chief organic acids of tobacco leaf—malic, citric and oxalic acids—undergo very little change in absolute amount during culture of the leaves in the light, although extensive photosynthesis occurs. The total organic acidity also remains essentially constant. During culture in the dark the amount of malic acid diminishes and that of citric acid increases, other acids remaining unchanged. It is suggested that the additional citric acid is formed directly from the malic acid. S. G. S.

Metabolism of the Proteins of Different Parts of the Wheat Grain compared with that of Casein. H. Jordan. (*Z. Unters. Lebensm.*, 1936, **72**, 457–460.)—Kaping (*Z. Unters. Lebensm.*, 1936, **72**, 453), by determining the ratio of carbon to nitrogen and of "vacat-oxygen"* to nitrogen in urine, compared the metabolic functions of the proteins of wheat gluten with those of casein. The investigation has been extended to the proteins in the separate parts of the wheat grain, *viz.* the germ, the flour and the bran. According to Kaping (*loc. cit.*) gluten protein approximates most nearly in feeding value to casein. If, however, the feeding is continued for a long period, with gluten as the source of nitrogen in the diet, the nutritional value in comparison with casein diminishes and the body-weight, which remains constant for a time, ultimately shows a slight diminution. The nitrogen balance also shows that slightly less nitrogen is being retained than with a casein diet. In the author's experiments, which were confined to periods of one week, the nitrogen absorption with casein diets and gluten diets showed little difference, the C : N and "vacat-O" : N ratios in urine being almost identical. The procedure consisted in feeding rats with diets the ingredients of which were identical, except that different proteins were used as the source of nitrogen. The constant ingredients of the diets were cod-liver oil, sugar, potato starch, mineral salts, orange juice and water. The variable sources of nitrogen were casein, wheat germ, wheat gluten (in the form of a commercial preparation "Glidin"), wheat bran and egg albumin. Each diet contained approximately the same amount of protein (9·4 per cent. on the dry substance) and had an energy value of 47 calories per animal. The urine and faeces were collected and analysed, the following determinations being made and expressed as an average value per animal per day:—urine carbon, urine "vacat-oxygen," urine nitrogen and faeces nitrogen. From these were calculated the ratio of carbon to nitrogen and of "vacat-oxygen" to nitrogen, and the nitrogen balance was determined. Nitrogen was determined by a semi-micro Kjeldahl method, carbon by the microchemical method of Nicloux-Osuka (Osuka, *Biochem. Z.*, 1932, **244**, 284), and the "vacat-oxygen" by the microchemical method of Müller-Kanitz (*Biochem. Z.*, 1932, **249**, 234). The results of the experiments were as follows:—The nitrogen balance was almost

* "Vacat-oxygen" is a measure of the oxidisable substances in urine which can be determined by reduction of iodic acid (Kaping, *Z. Unters. Lebensm.*, 1936, **72**, 455).

equal in all experiments, except that with wheat bran as the source of nitrogen it was higher than with other proteins. The nitrogen in the faeces was highest on the diet containing wheat germ, then followed the bran diet, the remaining diets yielding almost equal amounts of faecal nitrogen. With wheat germ diet the urinary quotients were distinctly higher, and highest of all with the bran diet. Similar experiments by Bickel, Sander and Schilling (*Münch. Med. Woch.*, **1935**, **37**, 1482) show that these high values are also given by rye bran. The amount of dry faeces was highest on the bran diet. This is due to the high cellulose-content of bran. The amount of faeces on the wheat germ diet, although less than on the bran diet, was higher than on the other diets; apparently the commercial germ preparation used contained much cellulose. The experiments show that when the proteins of the different parts of the wheat grain are used as the sole source of nitrogen in a balanced diet, the urinary quotients show different values.

A. O. J.

Nutritive Value of Bread. A. L. Baker, M. D. Wright and J. C. Drummond. (*J. Soc. Chem. Ind.*, **1937**, **56**, 191T–194T.)—The nutritive value of bread was studied with regard to its content of vitamin *B*, and particularly of the component B_1. Wheat itself from various sources contained between 2·0 and 2·5 units of vitamin B_1 per g. In stone-ground wholemeal flour 64 per cent. of the original vitamin B_1 in the wheat was found in the flour, about 13 per cent. in the bran, and 23 per cent. in the middlings. Flour from a modern mill contained 5 per cent. of the original vitamin B_1 in the flour, 70 per cent. in the sharps, 19 per cent. in the bran, and 6 per cent. in the germ. Samples of bread showed a wide range of values—from London white bread at 0·14 unit per g. to wholemeal bread at 1·2 units per g. Germ-bread contained 1·7 units per g. From enquiries made by the authors they have calculated that wholemeal bread constitutes about 18 per cent. of the total bread consumption of well-to-do families, but only about 5 per cent. of that of poor families, and since bread is the staple food of the poorer classes, a vitamin B_1 deficiency is to be anticipated amongst these people. The authors are engaged in a survey of the medical literature in order to ascertain if the commonly occurring disorders, such as constipation and gastric troubles, can be correlated with the decrease of vitamin B_1 ingested in bread, as compared with that a century ago. (See also succeeding abstract.) S. G. S.

Vitamin B_1 Content of Bread and Flour. L. J. Harris and P. C. Leong. (*J. Soc. Chem. Ind.*, **1937**, **56**, 195T–196T.) (See also preceding abstract.)—Various kinds of bread and flour were examined for vitamin B_1 content. The results indicated that commercial white bread contained 0·15 unit per g., "germ" bread 0·8 unit per g., and proprietary wholemeal bread 0·75 unit per g. Wholemeal bread from an experimental bakery contained 0·9 unit per g., "with germ" brown bread from the same source 0·8 to 0·9 unit per g., "without germ" brown bread 0·65 to 0·8 unit per g., and "bran" bread 0·5 unit per g. Flours ranged from 0·2 unit per g. for white flour to 1·5 units per g. for wholemeal; wheat germ contained from 6·0 to 9·6 units per g. The authors conclude that "bran" bread or brown bread without the germ is not much inferior to genuine wholemeal bread, and is greatly superior to white bread in its vitamin B_1 content. "Germ" bread

and "germ" flour are less potent than might have been imagined and are but little superior to ordinary wholemeal. Soil treatment appears to have little significant effect on the vitamin B_1 content of wheat or barley (Harris, *J. Agric. Sci.*, 1934, **24**, 410). S. G. S.

Reactions of Ascorbic Acid. G. Woker and I. Antener. (*Helv. Chim. Acta*, 1937, **20**, 732–741.)—The similarity between ascorbic acid and Schardinger's enzyme has been reported previously (*Helv. Chim. Acta*, 1937, **20**, 144; Abst., ANALYST, 1937, 321). The present paper describes the reactions between ascorbic acid and various reagents. Ascorbic acid reduced a solution of picric acid and picrate to picramic acid in the cold. Other reducing substances commonly present with ascorbic acid (glutathione, cystein and creatinine) reduce the mixture only on warming. The reduction of iodate to hydriodic acid by ascorbic acid is already known. The hydriodic acid will react with excess of iodate to liberate free iodine, which can be made to oxidise benzidine to benzidine blue. This can be made the basis of a quantitative test, and the limit for the reaction is 0·0000172 g. of ascorbic acid. It is possible that this reaction may be utilised for the estimation of thyroxine. Ascorbic acid will reduce quinone to quinhydrone and, in addition, will give the furfural reaction with a suitable redox system. Dehydroascorbic acid will react in a similar manner to give β- or β'-hydroxyfurfural. A green colour is obtained with orcinol in pure nitric acid and a yellowish-orange colour with phloroglucinol in the same acid. The limits of the reactions are 0·000176 g. and 0·000035 g. of ascorbic acid respectively. A positive reaction is also obtained with α-naphthol (Molisch's reaction), with a limiting value of 0·0000176 g. of ascorbic acid. Dehydroascorbic acid reacts with phenylhydrazine to give an osazone.

S. G. S.

The Titration Method for Vitamin *C*. L. J. Harris. (*5th Internat. Tech. & Chem. Congress Agricult. Industries.*)—The points to be watched in the determination of vitamin *C* by titration with 2, 6-dichlorophenolindophenol are (*a*) that proteins should be removed and a clear solution obtained by means of grinding with sand and trichloroacetic acid, although this may be omitted with certain clear fruit juices; (*b*) that extraction should be carried through and the titration of the extract begun with as little delay as possible; (*c*) the solution should be titrated at an acid reaction, and (*d*) the titration end-point should be reached within two minutes. Previously reported interfering substances and various modifications of the method are described, but it is concluded that simple titration gives surprisingly accurate results without the necessity for further modifications and complications; and although theoretically the method is not absolutely specific, few exceptions are actually encountered in every-day experience. S. G. S.

"Ascorbic Acid Oxidase" in Relation to Copper. E. Stotz, C. J. Harrer and C. G. King. (*J. Biol. Chem.*, 1937, **119**, 511–522.)—The catalytic activity of squash and cauliflower juices on the oxidation of ascorbic acid, previously ascribed to a specific oxidase, is now stated to be due to the copper present in combination with protein material. Diethyldithiocarbamate, 8-hydroxyquinoline, pyridine and potassium thiocyanate, sodium cyanide, potassium ethylxanthate, potassium ferrocyanide and sodium sulphide acted as copper inhibitors

and produced nearly complete poisoning of the "enzymes" as well as of inorganic copper and copper-protein mixtures. These inhibitors did not affect the catalytic function of nicotine-haemochromogen in a manner that would suggest that this type of substance is responsible for the oxidation of ascorbic acid by cauliflower juice or "purified squash oxidase." The catalytic properties of copper are considerably altered by the presence of proteins. A mixture of copper and albumin exhibits the characteristic properties of the "enzymes," with an optimum *p*H similar to that of the "enzymes," being inactivated by heat and acids, and showing similar velocity reactions to the quantity of substrate. The type of union between copper and protein is similar to that in copper amide, biuret, and copper haematophorphyrin. Although the work described in this paper was done only with cauliflower juice, "purified squash oxidase," cucumber juice and cabbage juice, it is suggested that other "ascorbic acid oxidases" which have been described are not essentially different from these. S. G. S.

Bacteriological

Detection of *Microbacterium tuberculosis* in the Air and Dust by a Simple Technique. G. M. Eisenburg. (*Amer. J. Hyg.*, 1937, **24**, 138–146.)—The author proves experimentally that living virulent tubercle bacilli are present in the air and dust of tuberculous environments. The investigation comprised the examination of rooms in four hospitals. Sterile evaporating dishes, 10 cm. in diameter, containing 20 ml. of sterile saline, were placed in the four corners of each room for 7 days. The contents of each dish, with washings, were then centrifuged in a separate tube and concentrated to 1 ml. Smears were made from this concentrate and examined microscopically; the remainder was subjected to digestion with an equal volume of 2, 3 and 5 per cent. oxalic acid solution for 30 minutes at 37° C., and centrifuged for 10 minutes at 3000 r.p.m., and the sediment was washed with sterile saline and again centrifuged and concentrated to 1 ml. Cultures were then made from the resulting concentrates. The remainder of the concentrates from each institution were pooled, and several guinea-pigs were inoculated from each of the four groups. Four culture media were used, *viz.* those of Petroff, Petragagni, Corper and Uyei, and Sweany and Evanoff. The first three were found to be good and are given in order of merit. The last was found to be unsatisfactory inasmuch as it allowed contaminating micro-organisms to grow.

The results, which were remarkable, may be summarised as follows:—Number of rooms tested, 15; number of samples, 55; percentage of smears showing acid-alcohol-fast bacilli, 88; number of primary cultures, 230; per cent. lost by contamination, 39; number of primary cultures remaining, 140; percentage number of primary cultures showing tubercle bacilli, 47. It will thus be seen that a large number of positive results were obtained by microscopical examination, and it is suggested that possibly much has been overlooked by earlier investigators. The number of positive results obtained by culture, *viz.* 47 per cent., shows that a considerable number of the acid-alcohol-fast bacilli were living tubercle bacilli. All the guinea-pigs inoculated were infected with tubercle bacilli. Inoculations were also made from the pooled cultures (after sub-cultivation) from each institution. It is

suggested that the air and dust of tuberculous environments may constitute a potential menace to the health and well-being of healthy individuals in constant contact with them. D. R. W.

Measurement of the Size of Viruses by High-speed Centrifuging. J. McIntosh and F. R. Selbie. (*Brit. J. Exper. Path.*, 1937, **18**, 162–74.)—A description is given of the super-centrifuge employed. It is constructed on the principle of the spinning top of Henriot and Huguenard, the rotor actually having its bearings on a cushion of air. Essentially it consists of (1) a duralumin rotor taking four small tubes, 2 × 0·5 cm.; (2) a phosphor-bronze stator having a series of nine holes drilled obliquely, so as to allow the compressed air to emerge upwards and obliquely upon the grooved rotor; (3) an air-compression plant driven by a 4 h.p. electric motor and delivering 20 cb.ft. of air per minute at a pressure of 80 to 90 lbs. per sq. in. The speed attainable is over 60,000 r.p.m. The frequency of revolution is determined by a stroboscope consisting of a neon light worked at known frequency and controlled by an electrically driven tuning fork.

The determination of the size of the particles is carried out by plotting logarithms of the initial and final concentrations (C_o and C_τ) against time. The straight line obtained by joining C_o and C_τ makes the angle θ with the horizontal; this is called the angle of sedimentation, and it is a function of the velocity of sedimentation of the particles such that their mean diameter $D = K \times \sqrt{\tan \theta}$, where K is a constant varying with the speed of the centrifuge. K was evaluated by conducting a test with staphylococci of known mean diameter (0·8μ), and was found to be 268·3 at 10,000 r.p.m. and 67·08 at 40,000 r.p.m. In this way the mean sizes of many viruses were determined, and the results agreed closely with those obtained by ultra-filtration. With the viruses of vaccinia and pleuropneumonia the angle of sedimentation decreases with increased time of spinning, indicating more than normal variation in the size of particles. D. R. W.

Toxicological and Forensic

Distribution of Veronal among the Organs in a Case of Fatal Veronal Poisoning. J. F. Reith. (*Pharm. Weekblad*, 1937, **74**, 649–652.)—The body, which was that of a suicide, was dissected 2 days after death, and the organs were stored for 50 days in a refrigerator, after which they were examined by the method of Van Itallie and Steenhauer (ANALYST, 1921, **46**, 413). The following results show the amounts (in g.) of material used (*a*), and of veronal found (in mg.) (*b*), respectively, for the various organs:—(1) *Unabsorbed veronal*:—Large intestine, (*a*) 187, (*b*) 210; small intestine, (*a*) 250, (*b*) 300; duodenum, (*a*) 18, (*b*) 260; stomach, (*a*) 105, (*b*) 4750. If the first three results are doubled and added to the fourth, a total of 6290 mg. of unabsorbed veronal is obtained. (2) *Absorbed veronal*:—Urine, (*a*) 45, (*b*) 40; gall, (*a*) 3, (*b*) 20; brain, (*a*) 1200 (estimated), (*b*) 500; liver, (*a*) 1285, (*b*) 1020; spleen and 1 kidney, (*a*) 380, (*b*) 270; blood (contents of right chamber and *vena cava* mixed), (*a*) 6000 (estimated), (*b*) 2420. The total absorbed veronal was therefore 4270 mg., making a grand total of 10·56 g.; the fatal dose for an adult is given as 8 to 10 g. The results are compared with those of Van

Itallie and Steenhauer (*loc. cit.*), and stress is laid on the importance of an examination of all the organs and body fluids if it is desired to obtain accurate information whether the dose taken was sufficient to produce fatal results. J. G.

Determination of Alcohol in Blood, Post-Mortem. E. Kohn-Abrest and L. Truffert. (*Ann. Falsificat.*, 1937, **30**, 210–216.)—Methods such as those of Nicloux (*Bull. Soc. Chim. Biol.*, 1931, **13**, 857; 1934, **16**, 1314; 1936, **18**, 318) and Wilmark (*Biochem. Z.*, 1922, **131**, 473), depending upon the reduction of chromic acid, are excellent for determining alcohol in small amounts of fresh blood taken from the living subject, but have the disadvantage that, if the blood is decomposed, it is not certain that alcohol is the only volatile reducing agent present. The method here described, in which the alcohol is isolated, is applicable when relatively large amounts of blood are available and is valuable in forensic practice when the subject has been fatally injured, and the possibility of alcoholic intoxication is involved. By a series of distillations of blood or viscera the alcohol is obtained as an aqueous solution, and from this it is separated by the addition of anhydrous potassium carbonate. Coniver (*Thèse de la Faculté des Sciences de Dijon*, 1931) and Olszewski (*Travaux du Laboratoire de Toxicologie de la Préfecture de Police*, 1932) have shown that, unless the amount of alcohol is very small and the material is in an advanced stage of putrefaction, the supernatant layer thus obtained represents, with reasonable accuracy, the volume of alcohol present. For viscera the procedure is as follows:—The minced viscera (1000 g.) are distilled with 1 litre of water and 10 g. of tartaric acid, and 700 ml. of distillate are collected. A sixth part of the distillate is reserved for the detection of chloroform, alkyl halides, etc., and the remainder is re-distilled, 170 ml. of distillate being collected. Concentration is continued in the same manner, the volumes of the successive distillates collected being 60 ml., 25 ml. and 10 ml., and a proportionately smaller apparatus (which should be provided with a fractionating column) is used for each distillation. The final concentrate of 10 ml. is divided into two portions, one of which is examined for volatile poisons and the other for alcohol by the method described later. For blood the procedure is as follows:—One hundred ml. (or 50 ml. if the alcohol-content is high) of heart or pulmonary blood (preferably the former) are distilled with 250 ml. of saturated picric acid solution and 50 ml. of water in an apparatus made entirely of glass. To the distillate (150 ml.) 10 ml. of 10 per cent. sodium carbonate solution are added, and the mixture is distilled in a smaller apparatus, 80 ml. of distillate being collected. This, in turn, is reduced to a volume of 40 ml. The successive concentrations are then as follows, the figures in brackets denoting the size of the distillation flask from which the distillate should be obtained:—25 ml. (100 ml.), 12 ml. (75 ml.), 6 ml. (40 ml.), 5 ml. (25 ml.), 2·5 ml. (15 ml.). When the 40-ml. distillate has been collected the graduated receiver is rinsed into the next distillation flask with 10 ml. of water and replaced by a smaller one. Similarly, after the 6-ml. distillate has been collected, the receiver is rinsed with 4 ml. of water and replaced by a still smaller one. The eighth concentrate (2·5 ml.) is placed in a special flask of 5 to 6 ml. capacity, the lower part of which is elongated into a narrow tube graduated in 1/100th ml. and, by means of a suitable funnel, 3 g. of anhydrous potassium carbonate and a trace of solid phenolphthalein

are added. The vessel is then filled with saturated potassium carbonate solution, stoppered and placed vertically with the graduated portion upwards. The alcohol, coloured red by the phenolphthalein, collects above the colourless aqueous layer and, when separation is complete, its volume is read and 0·02 ml. is added as a correction. The presence of phenolphthalein is essential when the alcohol-content is low and separation is consequently slow. Copper sulphate may be used instead of phenolphthalein, the alcohol layer then being colourless and the aqueous layer blue. The precision of the method has been verified by determining known amounts of alcohol in decomposed blood. By using 100 ml. of blood 0·4 part of alcohol per thousand can be determined. Pig's blood, kept in a closed vessel for 9 days at 18° to 22° C., gave no trace of alcohol. Viscera that had been kept in ice for two months before analysis gave 3·6 parts per thousand by vol. of reducing substances, expressed as alcohol, and 2·0 parts of alcohol separated by this method. The blood was then kept at room temperature for another month, after which it was found to contain 0·9 part of alcohol per thousand. The tendency, therefore, is for alcohol to disappear as putrefaction proceeds. A. O. J.

Water

Use of Activated Carbon in the Determination of Nitrate, Nitrite and Ammonia in Water and Sewage. G. Gad. (*Gas- u. Wasserfach*, 1936, **79**, 166; *Dept. Sci. Ind. Research—Water Pollution Res., Abstracts*, 1937, **10**, 15).—Activated carbon adsorbs nitrates and nitrites from acid, neutral and weakly alkaline solutions (*p*H 4·5 to 7·4), but not from more alkaline solutions (*p*H 8·5). It may therefore be used for removing turbidity and colour from water and sewage in which nitrate and nitrite are to be determined, provided that the sample is distinctly alkaline. The carbon should be purified by boiling with soda lye, washing with water and dilute hydrochloric acid, and drying. The water under examination should be made alkaline with sodium hydroxide (about 0·1 g. per 100 ml.) before being shaken with the carbon. Purified activated carbon may also be used for removing colour and turbidity (also hydrogen sulphide) from water in which ammonia is to be determined with Nessler's reagent. The sample is acidified with sulphuric or nitric acid, shaken with the carbon and filtered. Colour and turbidity cannot be sufficiently reduced by addition of cadmium acetate alone.

Agricultural

Distinction of Derris and *Lonchocarpus* Powders. A. Diakonoff. (*Pharm. Weekblad*, 1937, **74**, 901–909.)—The ground root of *Lonchocarpus* (cubé or barbasco) sometimes occurs in derris sold as an insecticide, and as the rotenone-content of the matter soluble in ether indicates that the insecticidal power of the latter is 1·5 to 2 times greater than that of the former, such mixtures must be regarded as instances of adulteration. The microscopical characteristics, as observed after clearing in the usual way with chloral hydrate, are described, but they do not afford a trustworthy method of distinguishing between the two powders; the differences in colour and odour are also of no assistance where

mixtures are concerned. It is preferable to mount the specimen in water, when the granules of derris are distinguishable by their irregular (usually angular) shape and relatively small size; 3 or more angles are usually visible, and aggregates of 3 or 4 granules frequently occur and give the impression of a composite triangle or square. A small hilum, with 3 or 4 fine branches radiating from a single point, is frequently present. *Lonchocarpus* granules, on the other hand, are much larger and are usually circular or egg-shaped and regular in contour; they may also occur in groups (usually in pairs), and the granules then join along a flattened side, and so still preserve the appearance of a circle. The larger granules usually have a hilum which appears, as a rule, as a single irregular semi-circular line following the contour of the circumference of the granule; the radiating type of hilum also occurs occasionally. These characteristics are illustrated in the original paper. The following results for (*a*) derris and (*b*) *Lonchocarpus* were obtained by plotting the frequency curves of the sizes of the granules:—Number of measurements made, (*a*) 1063, (*b*) 1169; maximum and minimum sizes, (*a*) 2 to 17μ, (*b*) 3 to 28μ; mean sizes, (*a*) 6·38 ± 0·1μ, (*b*) 9·80 ± 0·2μ; mean error of a single determination, (*a*) 2·24, (*b*) 3·70μ; median, (*a*) 5·43, (*b*) 9·50μ. J. G.

Organic

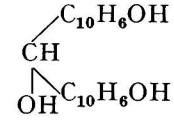
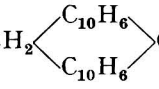
Selectivity of Iodic Acid in the Oxidation of Organic Compounds. R. J. Williams and M. A. Woods. (*J. Amer. Chem. Soc.*, 1937, **59**, 1408–1409.)—A search has been made for oxidising agents that might be sufficiently selective in action to make "partial oxidation equivalent analysis" (*J. Amer. Chem. Soc.*, 1937, **59**, 288, 291, 293) a useful method for determining structure, in that the determination of the amount of reagent used would yield definite information without isolation of oxidation products. Such selective oxidation is effected by treating 5 to 6 mg. of the organic compound with 10 ml. of a 1 per cent. solution of potassium iodate in 40 per cent. sulphuric acid and 2 ml. of water. The mixture is kept at 100° C. for 1½ hours, after which the liberated iodine is removed by steaming, and the unused iodate is determined by titration. When no visible iodine is liberated a titration gives the same results as a blank determination. All compounds obviously oxidised consumed at least 4 milli-equivalents of oxidising agent per millimole. The simple aliphatic alcohols tested (up to octyl alcohol) were oxidised except methanol, which was not oxidised in a sealed tube; polyhydric alcohols, such as glycol, glycerol, mannitol, inositol, etc., were not oxidised, but when the alcohol contained an unoxidised carbon atom in the alpha position to a hydroxyl group, as in trimethylene glycol, pinacol and propylene glycol, oxidation occurred. All the aliphatic and aromatic aldehydes tested were oxidised, as were also acetone, methyl-ethyl-ketone and acetophenone, but not benzophenone or benzil. Simple fatty acids (including formic acid) and aromatic acids gave negative results, as also did glycollic, lactic, tartaric, citric, mucic, mandelic and benzilic acids, and the unsaturated maleic and crotonic acids. Amino acids of protein origin (16 samples) were unoxidised, with the exception of cystine, tyrosine and tryptophane. All the aldohexoses and their derivatives tested gave negative results; a slight oxidation of cellobiose and trehalose was attributed to impurity.

Fructose, sorbose and sucrose were oxidised (the last-named probably owing to fructose formation), but benzoin was unaffected. The pentoses, *d*-arabinose and *l*-xylose (rhamnose more slowly) were oxidised, presumably owing to the formation of furfural. All the phenolic compounds tested (13), the phenol ethers, anisole and phenetole, and the 7 aniline derivatives tested were oxidised. D. G. H.

Use of Leucobases as Analytical Reagents. A. I. Matiu and C. Popesco. (*Bull. Soc. Chim.*, 1937, **4**, 1230–1235.)—The leucobase of methylene blue is oxidised in the air, but can be stabilised by forming the sulphone. An analytical reagent was made by treating 10 ml. of 0·1 per cent. aqueous methylene blue solution with 10 drops of 12 per cent. sodium thiosulphate solution and 20 drops of 1 per cent. hydrochloric acid. When shaken and allowed to stand for 5 to 15 minutes the mixture was completely decolorised. This thiosulphone reagent is stable in air for about 12 hours; strips of filter paper impregnated with it and dried in the dark are stable for about 24 hours. It can be used to distinguish oxidising from neutral or reducing media, giving a blue colour with oxidising solutions. Pancreatin gave a green-blue colour and a green precipitate, but pepsin, tyrosinase and yeast did not react. Most neutral inorganic salts are inactive, except those that have an oxidising action; with fixed alkalis, ammonia, potassium ferro- and ferricyanides, a blue colour is obtained; most reducing salts (sodium nitrite and hypophosphite are exceptions) are inert. E. M. P.

Detection of the Nitro Group in Organic Compounds. W. M. Hearon and R. G. Gustavson. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 352–353.)—A semi-micro test for the detection of nitro groups in organic compounds is based on the oxidation of ferrous to ferric hydroxide. The solutions required are:—(A) A solution of 25 g. of ferrous ammonium sulphate in 500 ml. of air-free water and 2 ml. of conc. sulphuric acid, and (B) alcoholic potassium hydroxide solution. Thirty g. of potassium hydroxide, dissolved in 30 ml. of water, are added to 200 ml. of 95 per cent. alcohol. *Method.*—Ten mg. of the finely-powdered organic substance are added to 0·7 ml. of (A) in a 4-ml. test-tube. After the addition of 0·5 ml. of (B) air is removed by means of a stream of inert gas, and the tube is quickly stoppered and shaken. In test analyses, all aromatic nitro compounds examined gave a brown precipitate in less than 30 seconds. Nitromethane, the only aliphatic compound tested, required 60 seconds. The reaction is not specific, but is also obtained with nitroso compounds, aliphatic nitrates and nitrites, quinones, and hydroxylamine. With these exceptions, seventy-five compounds not containing the nitro group gave negative results; many of them produced a light green precipitate, which in some instances became dark, owing to slight oxidation. Thus, when correlated with other tests, the reaction should be useful. It fails with highly coloured compounds. E. B. D.

Reactions between Formaldehyde and Naphthols. A. Castiglioni. (*Gazz. Chim. Ital.*, 1937, **67**, 324–326.)—When heated on the water-bath in the presence of conc. hydrochloric acid both α- and β-naphthols condense with formaldehyde to give a precipitate—red-brown with α-naphthol and red with β-naphthol.

On addition of alkali (preferably solid sodium hydroxide) the α-naphthol precipitate becomes azure blue, a reaction that will distinguish small quantities of the two naphthols when the red-brown and red precipitates are too similar in colour to be discriminated. With both naphthols the first condensation product is dinaphtholmethane; with α-naphthol this oxidises to dinaphtholcarbinol  with β-naphthol the dinaphtholmethane undergoes intramolecular condensation to give dinaphthopyran,  , m.p. 185° C. E. M. P.

Determination of Furfural and Methylfurfural in Mixtures. E. E. Hughes and S. F. Acree. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 318–321.)—At a temperature of 0° C. and under the same conditions, methylfurfural reacts more rapidly than furfural with bromine solution. Under the standard conditions of Hughes and Acree (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 123; Abst., ANALYST, 1934, **59**, 430) furfural reacts quantitatively with bromine in equimolecular proportions in 5 minutes, and further change is almost negligible after 1 hour. The rate of reaction of methylfurfural has been studied and the values for molecular consumption of bromine after different periods of time have been calculated. Hence, if duplicate solutions of a mixture of these aldehydes are made to react with equal amounts of bromine for different periods of time and the consumption of bromine by each is determined, the composition of the mixture may be found by means of the following formulae:

$$m = (0{\cdot}055)\,\frac{a_1x_2 - a_2x_1}{a_1b_2 - a_2b_1}$$

$$f = (0{\cdot}048)\,\frac{b_1x_2 - b_2x_1}{a_1b_2 - a_2b_1}$$

where m represents grams of methylfurfural, f grams of furfural, x_1 and x_2 are the total milli-equivalents of bromine consumed after periods t_1 and t_2, and a_1, a_2, b_1, b_2 are the molecular consumptions of bromine by furfural and methylfurfural respectively for the same periods of time. When $t_1 = 5$ minutes and $t_2 = 10$ minutes, $a_1 = a_2 = 1{\cdot}00$, $b_1 = 1{\cdot}38$, and $b_2 = 1{\cdot}63$. The method used is that of Hughes and Acree (*loc. cit.*). Their side-arm titration flask is described in a later paper (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 292; Abst., ANALYST, 1934, **59**, 712); it now has thermometer wells, extending into the solution, attached to each stopper of the flask. The temperature is maintained at 0 to 0·5° C. throughout the determination. The reagents are (i) 25 ml. of $N/10$ potassium bromate solution, containing potassium bromide, (ii) 10 ml. of 10 per cent. potassium iodide solution, (iii) 200 ml. of N hydrochloric acid, in which the sample containing the aldehydes is dissolved. In test analyses the mean error in the results was about 0·5 mg. with samples containing from 3 to 50 mg. of methylfurfural. E. B. D.

Wax-like Constituents of the Cherry, *Prunus avium* L. K. S. Markley and C. E. Sando. (*J. Biol. Chem.*, 1937, **119**, 641–645.)—Solid fatty acids, liquid fatty acids, glycerol and hydrocarbons have been obtained from a petroleum spirit extract of the skins of Bing cherries (*Prunus avium* L.). The solid fatty acids consisted of palmitic, stearic and a small amount of an acid higher than C_{18}; the liquid acids were linolic and oleic, and the hydrocarbons consisted chiefly of nonocosane together with one of a greater chain length. An ethereal extract of the skins yielded α-glucosido-sitosterol and ursolic acid. The yield of the petroleum spirit extract was 0·8 per cent. and that of the ethereal extract 0·1 per cent. of the dried skin. A comparison of these figures with the previously reported yields from apple and pear cuticles, *viz.* apple 3·24 and 4·61 per cent., and pear 1·95 and 2·38 per cent. for the petroleum spirit and following ethereal extracts, respectively (*J. Biol. Chem.*, 1935, **111**, 133; Abst., ANALYST, 1935, **60**, 767), suggests an explanation for the less efficient protective surface coating of the cherry. S. G. S.

Diphenylguanidine as a Standard in Neutralisation Processes. W. M. Thornton and C. L. Christ. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 339.)—In test analyses with diphenylguanidine as an original standard in acidimetry and alkalimetry, Carlton (*J. Amer. Chem. Soc.*, 1922, **44**, 1469–1474; Abst., ANALYST, 1922, **47**, 408), obtained excellent results, but this has not been the experience of other chemists. The authors have titrated diphenylguanidine with approximately $N/10$ hydrochloric acid, using Carlton's double indicator (bromophenol blue and methyl red), which gave a sharp end-point. The mean factor in four titrations was 0·10114 N. The acid had been prepared by diluting a measured amount of hydrochloric acid of constant b.p. to the required volume, and the factor calculated from this was 0·10058 N. Gravimetric analysis, in which the chloride was precipitated with silver nitrate, gave factors of 0·10054 N and 0·10049 N. The diphenylguanidine had been purified by Carlton's method (*loc. cit.*). Further research is being carried out on the preparation of pure diphenylguanidine and also of triphenylguanidine (*cf.* Callan and Strafford, *J. Soc. Chem. Ind.*, 1924, **43**, 1T). E. B. D.

Inorganic

Determination of Cadmium in Tin-rich Alloys by Loss in Weight. D. Hanson and W. T. Pell-Walpole. (*Tech. Publ. Internat. Tin Research and Dev. Council*, Series A, No. 55, 1937.)—Volatilisation of cadmium from alloys rich in tin can be made so complete without appreciable loss of tin that it is proposed as a method of analysis. A 3-g. sample of the alloy in a porcelain boat is placed in a silica tube closed at one end and connected with a vacuum pump at the other end. The tube is heated at 700° to 730° C. for 30 minutes. A high vacuum in the tube is unnecessary, reduction of pressure to 1 mm. of mercury having been found satisfactory. The evacuated tube is removed from the furnace and allowed to cool below the melting-point temperature of tin before air is admitted. The sample is then removed and weighed when cold, the loss in weight being taken as the cadmium-content. Results very close to the intended composition were obtained with

(*a*) binary alloys containing 0·25 to 50·0 per cent. of cadmium in tin and (*b*) ternary alloys containing similar amounts of cadmium in tin with 2 to 14 per cent. of antimony. Neither pure tin nor tin alloyed with 14 per cent. of antimony was found to lose weight under the above-mentioned conditions. S. G. C.

Determination of Arsenic in Tin. B. Tougarinoff. (*Bull. Soc. Chim. Belg.*, 1937, **46**, 141–170.)—A detailed study has been made of the methods for the determination of small quantities of arsenic in refined tin, based either on distillation as arsenic trichloride or evolution of arsine, and described in the literature (Lunge-Berl; *Ausgewählte Methoden*; American Society for Testing Materials; Villavecchia). Both methods were found to give reliable results; in the evolution method a correction of 0·2 to 0·3 mg. has to be made for the quantity of arsenic not volatilised as arsine. W. R. S.

Specific Reagent for the Determination and Separation of Thallium. R. Berg and E. S. Fahrenkamp. (*Z. anal. Chem.*, 1937, **109**, 305–315.)—The reagent is the β-aminonaphthalide of thioglycollic acid, $C_{10}H_7NH.CO.CH_2.SH$, in which the hydrogen atom of the SH-group is replaceable by metals. Precipitation of thallium is specific in alkaline tartrate solution containing cyanide, the complex $Tl(C_{12}H_{10}ONS)$ forming a lemon-yellow, crystalline precipitate containing 48·60 per cent. of thallium. The sulphate solution is neutralised with 2 *N* sodium hydroxide solution, treated with 2 g. of sodium tartrate, 3 to 5 g. of potassium cyanide, and 10 to 20 ml. of 2 *N* sodium hydroxide solution, and diluted to 100 ml. Precipitation is carried out in the cold with 4 to 5 times the theoretical amount of reagent in concentrated acetone solution. The amorphous precipitate becomes crystalline when the solution is stirred and boiled. The vessel is cooled in water, and the liquid is filtered through a porous glass crucible (G4); the precipitate is washed with cold water until free from cyanide and then with acetone to remove excess of reagent, and dried to constant weight at 100° C.

For the separation of thallium from other metals the following solutions are required:—a freshly made 5 per cent. solution of the reagent in acetone (it decomposes after a few hours); sodium tartrate solution, 20 per cent.; potassium cyanide solution, 20 per cent.; 2 *N* sodium hydroxide solution. The thallium solution (100 ml.) is treated with 10 to 25 ml. of tartrate solution and neutralised towards phenolphthalein with the alkali. Sufficient cyanide solution is added to make the final concentration 5 per cent. The alkalinity is then raised to normality by the addition of alkali. Precipitation is effected exactly as described above; the precipitate should not be compressed too strongly by suction, otherwise washing is less effective.

If iron is present, the ferricyanide formed should be reduced to ferrocyanide by means of hydroxylamine. Vanadate should be similarly reduced to vanadyl salt. Uranyl salts are kept in solution by the addition of ammonium carbonate, and by washing the precipitate with 10 per cent. ammonium carbonate solution, followed by water and acetone. In the presence of mercury, bismuth or lead, the thallium should be precipitated with a tenfold excess of reagent dissolved in sufficient acetone to provide a 30 per cent. concentration of the solvent in the final

bulk of liquid; mercury also requires 9 g. of cyanide per 100 ml. of final liquor. The carbonates of the alkaline earths, as well as magnesium hydroxide, are insoluble in alkaline cyanide solution, but these elements can be separated from thallium by substituting ammonia for 2 *N* sodium hydroxide in the procedure described. W. R. S.

Gravimetric Determination of Zinc by means of Anthranilic Acid. E. A. Ostroumow. (*Ann. Chim. anal.*, 1937, **19**, 173–176.)—Funk and Ditt's method (*Z. anal. Chem.*, 1933, **91**, 332; Abst., ANALYST, 1933, **58**, 241), applied as follows, is recommended. The slightly acid solution of zinc, from which metals other than those of the alkalis or alkaline earths are absent, is made slightly alkaline with sodium hydroxide and then acidified with a few drops of dilute acetic acid. Ammonium acetate should not be present. After dilution of the solution to about 150 to 200 ml. for each 0·1 g. of zinc present, an excess of sodium anthranilate solution is added slowly, with shaking, which is continued for 3 to 5 minutes. The precipitate of zinc anthranilate is filtered off after standing for about 20 minutes, washed first with dilute sodium anthranilate solution and then with alcohol, dried at 105 to 110° C., and weighed; 1 g. of the precipitate corresponds with 0·2411 g. of zinc oxide or 0·1937 g. of zinc. The reagent is prepared by dissolving 3 g. of anthranilic acid in dilute sodium hydroxide solution in amount just insufficient to neutralise the acid, and diluting the liquid to 100 ml. Quantitative results were obtained with pure solutions containing 0·05 g. of zinc. In order to apply the method it is, in general, necessary to effect a preliminary separation of the zinc as sulphide; the zinc sulphide precipitate is converted by heating into zinc oxide, which is dissolved in the minimum quantity of hydrochloric acid. S. G. C.

Sensitive Test for Manganese. E. Jensen. (*Z. anal. Chem.*, 1937, **109**, 178–181.)—The solution to be tested (1 ml.) is mixed with 2 ml. of strong hydrochloric acid and about 4 ml. of a mixture of equal volumes of ether and strong hydrochloric acid. A few small crystals of potassium chlorate added to the solution will give a green colour in a few seconds if manganese is present. The coloured compound is probably manganese trichloride. If less than 0·05 mg. of manganese per 10 ml. is present, the yellow colour of the liberated chlorine will mask the green tint. A more sensitive form of the test is as follows:—A few drops of the original solution are evaporated to dryness in a porcelain capsule. The warm residue is moistened with a few drops of strong nitric acid, cooled and treated with the mixture of ether and hydrochloric acid. This procedure will detect 0·005 mg. of manganese. The colour is stable for one-half to several hours. Metals yielding coloured solutions (nickel, copper, chromium, and especially cobalt) decrease the sensitiveness of the test. W. R. S.

Detection of Selenium. H. A. Ljung. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 328–330.)—When ammonium thiocyanate solution is added to a solution of selenious acid in hydrochloric acid and the mixture is boiled for 1 minute, a red precipitate of metallic selenium is obtained. For complete precipitation at least 4 mols. of ammonium thiocyanate per mol. of selenious acid are required, and the

acidity of the selenious solution should be not less than 6 *N* hydrochloric acid. With small quantities of selenium the reaction is complete after 20 to 30 seconds. If the amount of selenium present is very small, the precipitate remains in suspension for a considerable time, and its colour in reflected light varies from red through green and greenish-yellow to almost white as the concentration diminishes. The test is sensitive to 0·05 part of selenium per million in 7 *N* acid thiocyanate solution. If the mixture is allowed to stand for 48 hours after heating, the sensitivity is 1 part of selenium in 38 millions of 7 *N* hydrochloric acid solution. Ferrous, antimonious, and stannous ions interfere with the reaction. Attempts are being made to base a quantitative method on this reaction. E. B. D.

Determination of the Acids of Selenium and Arsenic in Presence of Each Other. J. Milbauer. (*Z. anal. Chem.*, 1937, **109**, 171–177.)—The following process was worked out for the determination of arsenate, arsenite, selenate and selenite in one and the same solution. (1) *Arsenate* is determined in the usual manner by precipitation with magnesia mixture. (2) *Arsenite* must be determined indirectly, by oxidation with ammoniacal hydrogen peroxide followed by precipitation with magnesia mixture, the excess of arsenic over that found under (1) being calculated to arsenite. (3) *Selenate* is precipitated as barium selenate in presence of perchloric acid. The solution is slightly acidified with 10 per cent. perchloric acid, treated with 2 drops of 10 per cent. silver perchlorate solution, heated to boiling, and stirred while being precipitated with 0·5 to 0·25*M* barium perchlorate solution added drop by drop. The precipitate is left to settle on the water-bath, collected next day in a porous porcelain crucible (A1 or A2) by means of its mother-liquor, and washed 4 times with portions of not more than 2 to 3 ml. of cold water. The barium selenate is dried to constant weight at 105° C. (4) *Selenite*, like arsenite, must be determined by an indirect procedure. This consists in reducing selenate and selenite to the element, calculating the selenate found under (3) into selenium, and the excess of selenium into selenite. A fresh aliquot portion of the original solution is acidified with 10 to 15 ml. of hydrochloric acid, diluted (300 to 400 ml.), treated with hydrazine sulphate, and gradually warmed on the water-bath. The reduction should be gradual, since otherwise the precipitate becomes contaminated with arsenic, as is shown by its collecting in voluminous dark flocks. Heating is continued until the selenium has deposited as a dark grey powder. This is collected in a porous porcelain crucible, washed with hot water and dried at 105° C. to constant weight. Molybdate mixture can only be used for concentrating traces of arsenic acid; the yellow precipitate is strongly contaminated with selenium compounds; these can be eliminated by precipitation of the arsenic acid with magnesia mixture. W. R. S.

Precipitation of Vanadates. E. Carrière and H. Guiter. (*Compt. rend.*, 1937, **204**, 1339–1340.)—A number of statements are made concerning the precipitation of metallic vanadates at different *p*H values. The addition of barium chloride to solutions containing the ammonium or sodium salts of vanadic acid, at *p*H 3·5 to 4·5, precipitates barium metavanadate $Ba(VO_3)_2$, the solubility of which is not sufficiently low to make it a useful precipitation form for gravimetric

analysis. At *p*H values between 4·5 and 10·8 a precipitate is produced having the composition $(BaO)_x(V_2O_5)$, where x varies between 1 and 3. The authors were unable to obtain a stage corresponding with the precipitation of barium pyrovanadate; thus Carnot's method, which is based on the precipitation of barium pyrovanate, did not appear capable of giving very accurate results. Between *p*H 10·8 and 11·4 barium orthovanadate is precipitated quantitatively, but has the drawback of being contaminated with barium carbonate, which also readily precipitates within this *p*H range. Silver metavanadate is precipitated from a solution containing acetic acid at *p*H 4 to 4·6. Lead orthovanadate, $Pb_3(VO_4)_2$, is precipitated from acetate solution at *p*H 4·3 to 5. The gravimetric determination of vanadates as lead vanadate is more accurate than as silver vanadate. S. G. C.

Microchemical

Microscopic Tests for Amino Acids. J. D. Surmatis and M. L. Willard. (*Mikrochem.*, 1937, **21**, 167–171.)—Amino acids react with reagents for alkaloids and solutions of salts of the heavy metals, frequently forming characteristic crystals which can be examined with a petrological microscope at 250×. For the tests a few crystals (less than 5 mg.) of the amino acid are dissolved in 20 per cent. hydrochloric acid, and the solution is neutralised with ammonium hydroxide (faint pink with phenolphthalein). Drops of the solution are treated with 10 per cent. solutions of the reagents on microscope slides. A precipitate is not formed immediately, but, as a rule, crystals appear on allowing the liquid to dry slowly. Nine specific tests are recorded for tyrosine and one for glycine (with Millon's reagent). Comparative tests were applied to glycine, cystine, tyrosine, alanine, glutamic acid, aspartic acid, leucine, phenylalanine and proline. The following reagents were tried: barium hydroxide, copper nitrate, lead acetate, magnesium hydroxide (results poor), Marmé's reagent, Mayer's reagent, mercuric chloride (only fair results), Millon's reagent, picric acid, picrolonic acid, platinic chloride (only fair results), potassium iodate, saccharin, silicotungstic acid, sodium nitroprusside (only fair results), tannic acid (only fair results), Wagner's reagent (only fair results), zinc hydroxide. Sixteen photomicrographs are given. J. W. M.

Microscopy of the Amino Acids and their Compounds. III. Copper Salts. B. Cunningham, M. MacIntyre and P. L. Kirk. (*Mikrochem.*, 1937, **21**, 245–247.)—The copper salts were prepared on the microscope slide by addition of solid cupric acetate to drops of solutions of the amino acids. Usually it was sufficient to prepare a saturated solution of the amino acid at room temperature. Many acids form more than one variety of crystals; generally two or more different forms appear in the same preparation, owing to local variation in conditions. In every instance the optical properties of one variety were investigated. The following form crystalline copper salts suitable for optical examination:—alanine, aspartic acid, cystine, glycine, isoleucine, leucine, lysine, methionine, nor-leucine, nor-valine, phenylalanine, serine, valine and α-amino-*n*-valeric acid. Most of these salts crystallised in thin bluish plates; a few formed needles. Sixteen photomicrographs are given. J. W. M.

Microchemical Reactions for Identifying Tellurium. G. Denigès. (*Compt. rend.*, 1937, **204**, 1256–1258.)—*Reaction with bromine.*—Minute particles (a fraction of a mg.) of the metalloid to be identified are placed on a glass slide and covered with two drops of a 20 per cent. solution of bromine in chloroform. When the liquid has spontaneously evaporated a yellow residue is left. This should appear quite dry. If it appears damp, the slide is warmed somewhat by passing it through the flame of a Bunsen burner and then allowing it to cool. One drop of a 2 : 1 mixture of chloroform and 95 per cent. alcohol is added, and the slide is placed on a surface heated to 35° to 40° C. in order to remove the solvents by evaporation. The residue is examined microscopically (×150 to 300). Tellurium is shown by the presence of a large number of more or less clear yellow hexahedral or octahedral crystals (sensitiveness of test: 0·05 mg.). *Reaction with iodine.*—To some particles (a fraction of a mg.) of the substance on a glass slide are added 3 or 4 drops of a 10 per cent. solution of iodine in alcohol (without potassium iodide). The drops are made to spread somewhat by manipulating the slide held in the hand. After about 1 minute, when the liquid has evaporated to a syrupy consistence, the slide is gently heated over a Bunsen flame in order to drive off most of the iodine. After cooling, the dry residue is examined microscopically (×150 to 300). Tellurium is shown by collections of small black crystals of tellurium iodide. These are soluble in alcohol and acetone, but insoluble in carbon tetrachloride. The halide compounds of tellurium are decomposed by ammonia, sodium hydroxide solution and dilute sulphuric and hydrochloric acids, giving solutions from which elemental tellurium can be precipitated by reducing agents.

S. G. C.

Microchemical References, 1936. (Supplement to *Mikrochem.*, 1936–37, **21**, 1–76.)—References are given in alphabetical order of the authors' names under the following headings. I. *Pure microchemistry*: (1) general and apparatus, 9 pages; (2) inorganic analysis, 8 pages; (3) organic analysis, 4 pages; (4) preparative, 1 page; (5) physical chemistry, 8 pages. II. *Applied microchemistry*: (1) biological chemistry, 9 pages; (2) medical and pharmaceutical chemistry, 8 pages; (3) mineralogical chemistry, 4 pages; (4) technical chemistry, 16 pages. Additions to previous volumes of microchemical references, 1931–1935, under the same headings, cover 27 pages; both the original reference and those of abstracts are given.

J. W. M.

Collected References. Micro-determination of Potassium. Ch. Cimerman and C. J. Rzymowska. (*Mikrochem.*, 1936, **20**, 129–143.) The 83 references include work published between 1929 and March, 1935, as references prior to 1929 have already been collected (*cf.* Heller, Haurowitz and Stary, "Alkali Metals," *Mikrochem.*, 1930, **8**, 182). The methods are described under the following headings:—Determination with (1) sodium cobaltihexanitrite, (2) chloroplatinic acid, (3) perchloric acid, (4) perrhenic acid, (5) zirconium sulphate, (6) tartaric acid, (7) organic reagents, (8) physico-chemical methods. The cobaltinitrite method (42 references), whether applied gravimetrically, volumetrically or colorimetrically, is the most recommended. Various authors give the error of the gravimetric method as 1 per cent.; filter sticks or Jena glass filters are used

for the filtration. The error of the method used colorimetrically is about 2 to 3 per cent.; this procedure is most suitable for rapid analysis and biological work. The platinic chloride method (8 references) may also be applied gravimetrically, volumetrically or colorimetrically. In the presence of large amounts of sodium it is best to precipitate the potassium first as the perchlorate or cobaltinitrite, and then to dissolve and re-precipitate it as the chloroplatinate. Errors may arise in washing the precipitate with alcohol containing a trace of aldehyde, which may cause a partial reduction of the compound. The perchlorate method (6 references) is less suited to microchemical work, owing to the solubility of the compound and its relatively small molecular weight; the perrhenic acid method is similar (2 references) and preferable because of the higher molecular weight of the reagent which, however, is rare and expensive. The zirconium sulphate method (2 references) is held to be as accurate as the perchlorate method; it may be applied nephelometrically. J. W. M.

Physical Methods, Apparatus, etc.

Sensitive Method for the Detection of Traces of Rare Earth Elements. M. Servigne. (*Compt. rend.*, 1937, **204**, 863–865.)—The method is an application of the results of the author's previous study of luminescence (*id.*, 1936, **203**, 1247). The finely divided substance is intimately mixed with a diluent, such as calcium tungstate, and sealed into a glass ampoule containing rarified gas and mercury vapour. Luminescence is brought about by exciting the interior of the ampoule with an electric discharge. The principle of the detection consists in the examination of the photo-luminescence spectrum, photographed on a panchromatic plate, for the principal rays of the element in question. It is stated that in this way it is possible to detect as little as 10^{-5} to 10^{-7} g. of elements such as samarium, dysprosium and europium in 1 g. of the mixture. Owing to the large surface exposed by the grains of the mixture, the sensitiveness of the method is much greater than that of an alternative photo-luminescence method in which the substance to be tested is dissolved in a small borax bead. S. G. C.

Micro-determination of Samarium by a Photo-luminescence Method. M. Servigne and E. Vassy. (*Compt. rend.*, 1937, **204**, 1566.)—The qualitative method referred to in the preceding abstract has been extended to give quantitative results, the principle being to compare the intensities of the same samarium emission band given by the sample and by a series of standards containing known amounts of samarium. Quantities of the order of 10^{-4} to 10^{-5} g. of the element can be determined, with an accuracy of 5 per cent. For details of the precautions required to ensure uniformity in working and of the technique required for the photometry of the spectra, the original paper should be consulted. S. G. C.

Spectrophotometric Determination of the Colour of Wine. A. Boutaric, L. Ferre and M. Roy. (*Ann. Falsificat.*, 1937, **30**, 196–209.)—To obtain reliable measurements of the colour of wine by the spectrophotometer, it was found necessary to use cells of less than 1 cm. in thickness, the actual thickness being measured to within 1/100th mm. The optical density $h = \mathrm{Log}_{10}\mathrm{I}_0/\mathrm{I}$ is then

calculated to a standard cell-thickness of 1 cm. For all the wines investigated, the absorption curves exhibited maximum values in the region of $520m\mu$ and, since this is the region to which the human eye is most sensitive, the optical density is a measure of the opacity of the wine. The ratio of the optical density h_1 at $480m\mu$ to the optical density h_2 at $640m\mu$, serves as a useful measure of the colour of the wine, h_1 being a measure of the opacity to blue light and h_2 of the opacity to red light. To prevent deposition of the colouring matter in the investigation of the effect of dilution upon colour, the diluent used was an aqueous, 15 per cent. by volume, solution of alcohol. According to Beer's Law, if n is the coefficient of dilution (*i.e.* the volume containing 1 ml. of the original wine) and h the optical density, the product nh, should be constant for a given wine. It was found that, for all wave-lengths, the value of nh diminishes in a non-linear manner, at first rapidly and then more slowly, as n increases. On diluting the wine with water and determining the optical density rapidly before the colouring matter separated, slightly different results were obtained, but these, again, were in disagreement with Beer's Law. A solution in 50 per cent. alcohol, of the colouring matter of the grapes from which one of the wines (Oberlin) was prepared, was found to obey Beer's Law. The explanation suggested is that, in the latter solution, the colouring matter exists in the form of simple molecules which are not greatly altered by dilution, whereas in the wine, the colour exists as complex micelles in equilibrium with the other constituents. When equilibrium is disturbed by dilution, the micelles break down into simpler bodies. It is generally assumed that the colour of a mixed wine may be calculated from the colours of its components by application of the mixture rule. Experiments showed, however, that this is only approximately true, the deviation from the rule being small for wave-lengths of $640m\mu$ and $480m\mu$, but considerable at $520m\mu$, the region of the characteristic colour of wine. To determine the effect of neutralisation upon the colour of wine, the pH and absorption curves were determined for samples of wines to which increasing amounts of sodium hydroxide solution had been added. The results show that, proportionally as the pH increases, (1) a minimum appears in the absorption curve at $480m\mu$ and at the same time the maximum is displaced towards the red, and (2) the ratio h_1/h_2 of the optical densities for the wave-lengths $480m\mu$ and $640m\mu$ diminishes, showing that the transmitted light becomes increasingly richer in light of short wave-length. A. O. J.

Amorphous Part of Starch in Fresh Bread and in Fresh Pastes and Solutions of Starch. J. R. Katz. (*Rec. Trav. Chim. Pays-Bas*, 1937, **56**, 785–793.)—The X-ray spectrogram of the white precipitate formed by dehydration of a 5 to 10 per cent. starch paste by rapid addition of a 20-fold quantity of 96 per cent. alcohol, is known as the "V-pattern" (*cf.* J. R. Katz and A. Weidinger, *id.*, 1934, **53**, 949). It is now considered to be the result of the superimposition of the amorphous pattern of starch and a purely crystalline V-pattern. If this is correct, the change in the starch during the staling of bread may be explained as being due to the crystallisation of the amorphous portion of the swollen granules. The micelles in fresh dilute starch paste or solutions are, therefore, mainly amorphous, whilst in concentrated pastes or solutions they may be partly crystalline and will therefore

produce a V-pattern. These spectrograms also indicate that a compound of starch and alkali is present in starch pastes which have been gelatinised by alkali at room temperature, and then rapidly precipitated with alcohol. If the alkali is subsequently removed by washing thoroughly with acid, a V-pattern is obtained, indicating that the above-mentioned compound has been split up. An analogy between these phenomena and the mercerisation of cellulose may be traced (*cf. Z. physik. Chem.*, A., 1930, **150**, 37, 60, 81). J. G.

Efficient Fractionation Equipment for the Qualitative and Quantitative Examination of Natural Fats. H. E. Longenecker. (*J. Soc. Chem. Ind.*, 1937, **56**, 199–202T.)—In order to effect the maximum separation of ester mixtures, an electrically-heated packed column has been devised, in which the rate of distillation can be adjusted. The Pyrex column, which is 90 cm. high and 17 mm. in internal diameter, is packed with single-turn glass helices for a length of 60 cm. It is heated by 15 ft. of nichrome wire (No. 22) wound on a piece of 25-mm. Pyrex tubing for the length of the packed distance, and the heating jacket is insulated by a Pyrex tube, 33 mm. in diameter. The temperature of the column, recorded by a thermometer inserted between the column and heated jacket, is controlled by external fixed and variable resistances. The still-head at the top of the column encloses a thermometer, and collection of the distillate is regulated by a stop-cock (2 mm.) below the condenser, with a separate connection for maintenance of low pressures or release of pressure when the stop-cock is closed. Except towards the end of distillation, the temperature of the vapour at the top of the column should approximate to that of the b.p. of the material being collected, and should be an index of the efficiency of fractionation. The temperature rise for adjacent members of the fatty acid series is about 15° to 20° C., according to the pressure (0·1 to 2 mm.). Maximum efficiency is obtained by so regulating the bath and column temperatures that there is never a visible accumulation of liquid in the packed length of the column. The stop-cock is kept closed at first and at frequent intervals during the collection of intermediate fractions, to enable equilibrium between liquid and vapour phases to be attained. A normal ester mixture obtained in the analysis of a relatively simple fat may be effectively separated when distilled at the rate of 20 to 25 g. per hour. Several sets of typical distillation data, including analyses of "solid" esters of beef tallow and butter-fat "liquid" esters, are given, and the use of the column for the qualitative and quantitative determination of minor components in natural fats is suggested. Thus the occurrence of small amounts of palmitoleic and myristic acids in arachis oil has been demonstrated. The fact that concordant results were obtained in the composite analysis of arachis oil by the use of this column and of a Willstätter bulb is interpreted as an indication of the general accuracy of ester fractionation procedure in the analysis of natural fats. D. G. H.

Reviews

TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS. By I. M. KOLTHOFF and E. B. SANDELL. Pp. 749. New York: The Macmillan Co. 1936. Price 20s.

This new work strikes one as a cross between two more usual types—one the book on practical analytical processes, and the other the book dealing with theoretical fundamentals and physico-chemical interpretation. The present book shows some of the best features of both, and is thoroughly up-to-date. One gets the impression at first that over-much space is taken up with the theoretical aspects, but in reality the treatment is well balanced, for it is divided evenly between the fundamental theories of the subject, the practical methods of working and the more important methods of analysis. The authors maintain that the important end is to familiarise the student with the procedures of analysis, and to awaken a sense of proportion in his work. For example, in an excellent chapter on errors in quantitative analysis (pp. 250–278), it is stated: "Obviously it is a waste of time and labour to determine a constituent with great accuracy, even when this is possible, if there is no particular demand for a very accurate result . . . it is all a matter of commonsense; the analyst must possess a sense of values." However, for the most part, special attention is paid to procedures capable of giving high accuracy. "The analyst who can perform accurate analyses and who has a grasp of the factors involved . . . will understand what legitimate changes can be made in a procedure when results of lesser accuracy are satisfactory."

The book is divided into four chief sections: gravimetric analysis (about 400 pages), volumetric analysis (about 200 pages), physico-chemical methods (about 45 pages), and the analysis of complex materials (brass, steel, silicate rocks, about 60 pages). The first two sections are subdivided into theoretical and practical parts. The theoretical matters are discussed to quite an advanced stage, usually with reference to so-called typical examples. As a result of a discussion of the factors affecting the formation and properties of precipitates, the interesting conclusion is reached that the purest precipitate can often be obtained in the following way: "The precipitation is made at room temperature from concentrated solution; the suspension is diluted with water, or, better, with an electrolyte solution in which the precipitate is more soluble than in water (to promote speed of recrystallisation) and is digested overnight on a steam-bath." The situation, however, is so complex that this conclusion cannot be put indiscriminately into practical effect. In fact, when the authors come to describe precipitation methods, the more usual method of precipitating in a hot solution is frequently given, even for precipitates such as calcium oxalate, barium sulphate, and the like, for which it might be thought that the conclusion quoted above was readily applicable.

In the practical part, full descriptions of selected methods are given for a limited number of elements. There are useful examples in which the relative advantages of a classical method and a more modern method are contrasted, as, for instance, the hydroxide and the hydroxyquinoline methods for aluminium. The book does not set out to be encyclopaedic, although where a full description is

not given for the determination of a particular element, various methods are often briefly outlined or indicated by a literature reference. This system results in some elements not being dealt with very adequately—tin, for example; antimony is only mentioned in passing as being determined by potassium bromate, no directions being given. In the volumetric part many instances occur of the use of the newer adsorption and oxidation-reduction indicators, standard ceric sulphate solution, and so on.

The numerous recent literature references add to the value of the book, but it was observed that British work is not very well represented. Among some minor slips is a statement (p. 496), made in connection with calibration of volumetric glassware, that 15° C. is the standard temperature for calibration in England, whereas the B.S.I. have for some time past adopted 20° C.; this, however, does not affect the usefulness of the calibration table given, since this is based on a standard temperature of 20° C., the temperature used in the United States. It is implied (p. 545) that zinc can be determined in the same way as nickel by cyanide—silver nitrate titration; this would not appear to be correct in view of the ready dissociation of the zinc-cyanide complex compared with the nickel-cyanide complex. The statement (p. 606) that quadrivalent tin is reduced by metallic iron, lead and zinc to the bivalent form is incorrect for zinc, which usually reduces it to metal. The very few slips seen indicate the great care taken with the preparation as a whole. An excellent feature is provided by the lists of questions appended to each chapter. There are good author- and subject-indexes.

At its moderate price the book should prove attractive to students, and, in fact, because of its modern treatment, to all concerned with inorganic analysis.

S. G. CLARKE

LE CONTRÔLE ANALYTIQUE DANS L'INDUSTRIE CHIMIQUE MINÉRALE. A. SANFOURCHE, Ing. Chim., D.ès Sc. Pp. 547. Paris: Masson et Cie. Price 120fr.

This book, written by the head of the central laboratory of the Compagnie de Saint Gobain, concerns itself exclusively with the control and examination of the products of the manufacture of inorganic chemicals. It is not, and does not pretend to be, a text-book of inorganic analysis, neither does it deal with analysis connected with metallurgy, ceramics, etc., but within its limitations it is a valuable laboratory manual. Descriptions of processes have a Gallic clarity which is not always to be found in text-books, and within its covers is a very large amount of analytical wisdom; whether this wisdom, once lost sight of, will readily be refound, is perhaps not quite so certain, as the index is not all that one might wish, and cross-references apparently do not exist.

The book is divided into four sections—"Generalities" (64 pp.), "Heavy Chemical Industry" (154 pp.), "Fertilizers" (109 pp.), and "Light Chemical Industry" (186 pp.); of these, the last gives the impression of being very much the weakest. While the great bulk of the methods are undoubtedly sound, and while the descriptions leave nothing to be desired, and the comments are admirable, one may perhaps be permitted occasionally to differ from the author as to the wisdom of certain procedures. The titration of thiosulphate with iodine on the assumption

that tetrathionate is the product (p. 436) seems to be at least of doubtful validity, and boiling off bromine from a hydrochloric acid solution of mercury (p. 527) would appear likely to result in some loss of mercury. The statement (p. 495) that one may reduce ferricyanide to ferrocyanide with ferrous sulphate is incomprehensible as it stands, and to say that "the separation of bromine from chlorine . . . has only received partial solution" (p. 358) argues a lack of acquaintance with the fairly large amount of work done in other countries. Apart, however, from these few criticisms, and taking the book for what it is intended to be—a guide to the examination of certain definite products—it is a manual of great value, and authoritative in that it seems to embody the established practice of the laboratory of a large chemical firm. Its great weakness, and one which cannot be guarded against, will probably be the change in stress on different impurities which is bound to occur with changing methods of manufacture.

The book is well bound, and the tables of factors with which it abounds should lead to considerable saving of time for those who use it. Proof reading appears to have been careful, though two or three slips are to be noticed. To English eyes the print seems rather pale and the paper rather transparent, but in neither respect unpleasantly so. It is the book of a man who is a master of his subject and who is not afraid to criticise official methods. B. S. EVANS

HANDBOOK OF CHEMISTRY AND PHYSICS. A READY-REFERENCE BOOK OF CHEMICAL AND PHYSICAL DATA. Edited by C. D. HODGMAN, M.S. Twenty-first Edition, 1936–7. Pp. xviii + 2020. Published by The Chemical Rubber Publishing Co., Cleveland, Ohio, U.S.A. Price 25s.

Only last year the twentieth edition of this useful little volume was noticed in THE ANALYST, and now the work may be said to have attained its "majority." It is substantially a book of tables—chemical, physical and mathematical, textual matter occupying less than one-tenth of the total space and consisting largely of definitions and brief explanations of fundamentals. The analyst will not go to it for descriptions of methods, but it is the kind of book to have always at hand in the laboratory or at the desk. The present edition contains 70 pages more than its predecessor. The new matter includes, besides some physical and mathematical data, a 17-page table of the properties of some commercial plastics, an extension of the section on Laboratory Arts and Recipes from 8 to 17 pages, a considerable extension of the photographic section, a list of isotopes (which now occupies 6 pages instead of 3), and one addition to the tables of densities of aqueous solutions—that of perchloric acid. No change appears to have been made since the last edition in the main tables of the physical properties of chemical compounds (about 400 pages).

The qualities of most importance in a book of this kind are reliability and handiness. The accuracy of the older matter may reasonably be taken for granted in a twenty-first edition, and if the absence of misprints and other patent errors is indicative of the care given to the selection of the newer matter, this also may be accepted with confidence. The reviewer has encountered no mistakes in the course of some months' use of the book. As to its handiness, its page size is small (4 by 6½ ins.), and, notwithstanding the use of thin paper, its 2000 pages make

it a rather stubby volume. Its limp cover and fine finish, however, render it very convenient to handle, and it will lie open at any page without any strain on the binding, but there is at times some inconvenience in reading to the middle of a double page. In a book to be read continuously this would become intolerable, but in a reference book it seems to the reviewer a minor inconvenience compared with that of having two volumes and finding that the wrong one usually comes to hand first, or that the index has to be consulted in one volume and the required matter in the other. J. H. LANE

BOOKS AND DOCUMENTS. By J. S. GRANT, Ph.D., F.I.C. Pp. xii + 218, with 36 illustrations, including 12 plates. London: Grafton & Co. 1937. Price 10s. 6d.

This volume is intended for the use of all who are engaged in any way in the manufacture, use and investigation of paper, inks and books, and although many readers may not find the whole text of interest, much will prove useful to the majority, and the author has met with considerable success in an ambitious attempt.

The subject-matter is divided into two parts, the first dealing with the dating of books and documents and including the history of paper-making, dating from the evidence provided by the paper, ink and other materials, chemical and physical tests (the latter illustrating the great value of filtered ultra-violet radiation for differentiation), and the detection of erasures, faded writing and ordinarily invisible inks. Part II contains a wealth of information on the permanence and preservation of books and documents from all points of view, tests for stability, the effects of light, heat, air and moisture, the selection of, and specifications for, papers and inks, and future methods for the production of permanent records. The volume is completed by a combined name and subject index which is both comprehensive and accurate.

Throughout the text there is evidence of the author's industry and care in compilation, and the abundant cross-references should ensure that the reader misses nothing relevant to the subject. In addition, a bibliography at the end of each chapter provides a guide to other books and scientific papers in which more detailed information may be found.

The illustrations in the text and the plates are good, with perhaps the exception of Fig. 36, but there is no obvious reason why a dissecting lens, two needles and a bottle should be displayed on a plate instead of as text figures. Since the illustrations are not arranged in strictly numerical order, reference to them would be facilitated by quoting the page in addition to the figure number of each.

On p. 45 the statement is made that "the various dating tests . . . can be used by workers having little or no knowledge of the methods of experimental chemistry or physics," and whilst this is certainly true, it would be a highly dangerous procedure to allow so ill-equipped a worker to operate on a document valuable on account of its age, rarity, or the likelihood of its becoming a court exhibit, for irremediable damage may easily be done. It is to be regretted that some of the chemical tests described do not justify the confidence which is often

placed in their results. Thus a blue colour on the addition of iodine solution, as described on p. 61, does not necessarily indicate the presence of starch, for the same reaction is given by some hydro-, oxy- and nitro-celluloses, saponins and other compounds liable to occur in or on paper. The Herzberg chlor-zinc iodine test described on p. 48 is widely used, but at the best gives uncertain results, and the reviewer has been greatly puzzled at times when, on applying the test, some fibres are coloured blue at one end and brown at the other. Many varieties of stylographic pens do not yield the type of stroke described on p. 40, for not infrequently one finds the track of the central wire as a darker line within the stroke, and some writers when using these pens habitually produce strokes of uneven thickness, especially when certain inks are used.

The proof reading has been carefully done, although a few minor errors have escaped correction. Thus on p. 65 Prussian blue is stated to yield a *blue* ash on ignition; "methylacetate" on p. 194 should evidently be preceded by the word "cellulose"; on p. 27 the spelling of "encyclopaedias" is rather mixed, whilst a little ambiguity about the storage of loose sheets occurs on p. 175, where presumably "flat" should be interpreted as "horizontally."

Within the limits of a comparatively small volume the author has included an abundance of diverse information and has produced a work which will merit a wide appeal. It will prove of distinct service to all interested in the preservation of books and documents—a subject of outstanding importance in the recording of a nation's activities.

T. J. WARD

AN INTRODUCTION TO ORGANIC CHEMISTRY. By ALEXANDER LOWY, Ph.D., and BENJAMIN HARROW, Ph.D. Pp. xiv + 429. Fourth Edition. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1936. Price 15s. net.

Introductions to organic chemistry are so numerous and, for the most part, so much alike that the mere sight of one is apt to cause a feeling of ennui. With Lowy and Harrow's book, however, this feeling, if it arises at all, is rapidly overwhelmed by one of eager interest which is maintained until the end, for although the traditional divisions of the subject (aliphatic, aromatic, heterocyclic, etc.) are adhered to, there are many features which do not commonly occur in text-books.

At the very beginning of the book the student, if he reads the introductory chapter, is made to realise that organic chemistry is not a useless subject, but one that enters into every phase of living activity, and throughout the text the authors lay stress on its connection with medicine, dentistry, agriculture, and industry—in short, the uses of compounds rather than their physical constants are recorded. In the body of the book are numerous charts summarising the manufacture, the derivatives or uses of the more important compounds. The human interest is also brought in by the inclusion, in appropriate places, of photographs of great organic chemists. To each photograph is attached a suitable biographical note. The inclusion of chapters on such subjects as "Foodstuffs and their Changes in the Body," "Dyes and Stains," and so on, also add to the interest of the book. The work ends with a chapter on nomenclature, an extensive list of special books, a glossary of unusual words (mostly medical) and an index.

The authors have included chapters on such advanced subjects as Enzymes, Vitamins and Hormones, Plant and Animal Pigments, and Vegetable Alkaloids. Even Schoenheimer's work on the use of heavy hydrogen in tracing the course of fat metabolism receives mention. In an elementary book such subjects must of necessity be inadequately treated (the alkaloids are dismissed in 3 pages), and although they are of great importance and absorbing interest, their inclusion tends to bewilder the elementary student.

American spelling, of course, is to be expected, but few British chemists will readily tolerate the terms mono, di and tri *atomic* alcohols.

Although readers with a deep knowledge of organic chemistry and very critical minds might be inclined to regard this book as superficial in some respects, yet it is well written and excellently produced. It presents the beginnings of organic chemistry in an unusually interesting way and cannot fail to arouse in the student a desire for more. HAROLD TOMS

STEDMAN'S MEDICAL DICTIONARY. Thirteenth Edition. By T. L. STEDMAN, A.M., M.D. Pp. xii + 1291. London: Baillière, Tindall & Cox. 1937. Price 35s.

Medicine is steadily tending to become a branch of applied biochemistry, and pathological conditions are now studied as manifestations of the sum of chemical reactions that have followed an abnormal course and require chemical control. A striking proof of this dependence of medicine upon chemistry is afforded by a comparison of this new edition of *Stedman's Medical Dictionary* with various standard medical dictionaries. In the present work drugs are defined in chemical terms, and chemical tests (*e.g.* the Reinsch test) are not merely mentioned, but also described in brief outline.

This exceptionally full treatment of the chemical side of medicine does not, however, involve neglect of the medical side, for the ground is thoroughly covered; one will find here fully explained both the common and the less known terms used in anatomy, pathology, medicine, surgery and pharmacology. There is also a useful introductory section on medical etymology and the correct method of word-building in medical science.

Bacteriology is fully dealt with, and there is an appendix of 15 pages, giving the morphology, cultural and staining properties, and pathogenicity of the principal pathogenic micro-organisms. Another appendix contains an alphabetical table of drugs, with their doses and therapeutic indications; this is based on the U.S. Pharmacopoeia XIth Revision, and the National Formulary, 6th Edition.

As the work is of American origin, transatlantic spelling has been adopted for certain words, such as "sulfur," for which, until recent years, American doctors used the English form, "sulphur."

To sum up, this dictionary will be found invaluable by biochemists who wish to follow the significance of technical papers in the medical press, and by medical men and veterinary surgeons who are alive to the chemical development of their subjects and wish to understand the meaning of chemical terms that are now in daily use. EDITOR