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THE ANALYST.

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

An ordinary meeting of the Society was held on Wednesday evening, June 7, in the Chemical Society's Rooms, Burlington House. The President, Mr. G. Embrey, F.I.C. occupied the chair.

The minutes of the previous ordinary meeting were read and confirmed.

The following papers were read: "Estimation of Pentoses or Pentosans by Means of Fehling's Solution," by Julian L. Baker, F.I.C., and H. F. E. Hulton, A.I.C.; "Potash and Other Mineral Fertilisers and Constituents of Plants," by R. R. Tatlock, F.I.C., and R. T. Thomson, F.I.C.; "Determination of the Reichert-Meissl and Polenske Figures of Butter and Margarine, using Small Quantities of the Fat," by A. Douglas Heywood, F.I.C.; "Calorific Valuation of Coal Without a Calorimeter," by H. Proctor Smith, F.I.C.; and "Estimation of Acetone in the Presence of Ethyl Alcohol," by Jitendranath Rakshit.

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MICROSCOPICAL METHODS: WITH SPECIAL REFERENCE TO THE EXAMINATION OF DRUGS.

By HENRY G. GREENISH, F.I.C.

(*Read at the Meeting, May* 3, 1916.)

I propose to deal with the subject-matter of my paper under the following heads:

1. Methods for the Identification of a Simple Powder;
2. Methods for the Determination of the Purity of a Simple Powder;
3. Methods for the Determination of the Composition of a Compound Powder;
4. Methods for Detecting Drug Powders under certain unusual Conditions.

1. *Methods for the Identification of a Simple Powder.*—The first step is a preliminary examination with an ordinary hand lens. Some of the powder is placed on a sheet of white paper, covered with another sheet, the surface flattened with a

paper-knife, and examined with a lens. Particles large enough to afford sections—*e.g.*, a millimetre square—are prepared as follows: A cylinder of elder-pith is cut in half longitudinally, the surface moistened with a mixture of gum and glycerol, and the particles to be cut are picked up and laid on the flat surface of the pith, just below the transverse end. After drying for a short time they are covered with the other half of the pith and the two halves tied together. The sections when cut are transferred at once to a slide, moistened with alcohol, and when the alcohol has nearly evaporated a solution of chloral hydrate is added.

A few of the larger particles are transferred to a slide, and gently warmed with 2 drops of solution of potash (about 10 to 20 per cent.). Then, by a sliding pressure on the coverslip, an attempt is made to separate the tissues so as to show the structure.

I seldom omit this preliminary examination without afterwards regretting it. It has rendered me good service, especially in the identification of unfamiliar drugs, and sections already referred to may be obtained from very small fragments.

The next step is the examination of the finer particles of the powder, or of the powder reduced to a sufficient degree of fineness to pass through a No. 60 or 80 sieve.

The best method now, and the one I almost invariably follow, is to take three hollowed glass blocks, place about 0·1 to 0·2 grm. of powder in each, and mix the first with water, the second with dilute glycerol, and the third with solution of chloral hydrate. The mixing is effected by stirring with a small glass rod, and is a little tedious with the water and dilute glycerol preparations. The mixtures should be so thick that the particles of powder do not sink, and, therefore, when a small portion is removed, an average of the bulk is taken. No specific quantities can be given, as some powders absorb much more liquid than others. Let these stand for about twelve hours.

It is advisable to examine the chloral preparation first. The solution of chloral hydrate will have dissolved starch, protoplasm, aleurone grains, etc., and will also have removed much of the colouring matter, so that the particles are well cleared and the examination of the structure much facilitated, particularly the structure of the larger and thicker fragments, and it is these that are usually the most difficult to deal with. It is preferable to examine the structure first, and deal with the cell-contents afterwards, as the interpretation of the water and dilute glycerol preparations is easier if the observer is acquainted with the nature of the elements present and with their arrangement in the larger particles.

The examination should be made with the low power first; indeed, it is surprising how much information the lower power will, with practice, afford. The high power should be used only for details not distinctly visible under the low power. Attention is directed first to conspicuous cells or tissues such as sclerenchymatous cells, bast-fibres, fragments of epidermis, hairs, etc. Then the larger fragments are examined, focussing the upper layer of cells first, and gradually proceeding through the fragment, an endeavour being made to form a mental picture of the structure. These fragments often lie in oblique positions, and are troublesome to interpret correctly; by touching the coverslip with a needle their position may be altered so that they exhibit their structure better. The examination of the sections

and of the potash preparations made at first may also throw light on the structure of these particles.

Another useful method of obtaining clear preparations from a powder is to mix about 0·1 grm. with 10 c.c. of a solution of chloral hydrate, transfer to a centrifuge tube, warm in a water-bath for about half an hour, centrifuge and pour off the solution, which is often very dark in colour; repeat the treatment with 5 c.c. of solution of chloral hydrate once or twice and use the final residue for examination.

If the powder to be examined is very dark in colour, as is the case with many barks, decolorisation with hypochlorite may be resorted to. One advantage of this method is that staining reactions for lignified and suberised membranes, callus plates, etc., may be applied to the bleached powder, and thereby the detection of these much facilitated. I have found the following method answer well: About 0·2 grm. of the powder is mixed with 10 c.c. of a solution of hypochlorite and occasionally shaken until most of the colour has been removed. The action must not be continued longer than is absolutely necessary, as the substances that produce lignin and other reactions may be destroyed and erroneous conclusions drawn. After centrifuging, the deposit is washed thoroughly with water and examined; it can be utilised also for the detection of lignified cell-walls (by phloroglucin and hydrochloric acid), of suberised and cuticularised membranes (by warming with solution of Soudan red, or by prolonged contact in the cold with tincture of alkanna diluted with an equal volume of water), or of callus plates (with corallin-soda).

When the structure of the powder has been thoroughly investigated, the preparations made with dilute glycerol and with water are examined. These preparations have the advantage of retaining, comparatively unaltered, the cell-contents and also the original colour; but as the particles are much less clear and transparent, they are more difficult to examine.

For the detection of starch I use a saturated solution of iodine in solution of chloral hydrate; this reagent clears the tissues and simultaneously stains the starch grains, which also slowly swell and gelatinise, thus rendering the identification of minute grains more easy; the solution also contains a fairly large proportion of iodine, which is an advantage in the case of those powders which absorb iodine somewhat freely.

For the detection of oil, tincture of alkanna is the best reagent. In making the tincture the crushed drug should first be exhausted by percolation with cold water, then dried and boiled with strong alcohol. I have found a tincture made in this way to be more permanent and to colour better than one made by simple maceration. A little of the tincture is diluted with an equal volume of water, the powder suspended in it for half an hour, then centrifuged and the deposit examined; or the staining may be carried out on the slide, in which case it should be kept in a damp atmosphere for half an hour.

For the detection of callus plates the bleached powder should be mounted in freshly made solution of corallin in aqueous sodium carbonate, the colour of the reagent being a bright but pale pink.

The best method for the detection of mucilage is to stain the original powder

with one of the three following reagents: (*a*) solution of ruthenium red in a solution of lead acetate; (*b*) corallin-soda; (*c*) saturated aqueous solution of Bismarck brown. For most mucilages the first-named reagent is the best: the mucilage stains a brilliant pink, which is very conspicuous, but some mucilages do not stain with it, and therefore it is advantageous to apply the other reagents as well.

Except for demonstration purposes, the practical histologist will seldom have occasion to make double stained preparations of vegetable powders. Should such occasion arise, then the following method (Cordonnier's) is the best.

One grm. of carmine and 5 grms. of alum are triturated with a little distilled water, the mixture evaporated to dryness at a gentle heat, allowed to stand for twenty-four hours, then dissolved in 100 c.c. of cold distilled water and filtered. Into a flask capable of holding 120 c.c. are introduced in the order named iodine green (Grübler) 0·1 grm. chloroform 1 grm., alum-carmine 100 c.c., and the mixture is shaken till dissolved, and is then filtered. One-tenth of a grm. of the powder is bleached with 10 c.c. of a solution of hypochlorite for about ten minutes, then separated by the centrifuge and washed with water until the hypochlorite is removed; the last washings are decanted and 5 c.c. of the double stain are added; after ten minutes the stain is diluted with water and the material washed several times in the centrifuge. The powder is then passed successively through 60 per cent. alcohol, 90 per cent. alcohol, absolute alcohol (twice), and xylol; finally a little of the mixed stained powder is added to a drop of Canada balsam on a slide, then well mixed, covered, pressed gently, and allowed to dry.

It is essential that sketches should be made of the structures and cell-contents observed. The best method is to outline these by means of the camera lucida, as by this means the relative sizes are correctly recorded, and absolute sizes may easily be determined by measuring the sketches. The details should be filled in without the camera. This is, in my opinion, far preferable to any photographic method. Photographic records have a certain value in providing a rapid record of such well-defined objects as sclerenchymatous cells, bast-fibres, and so on, but they are comparatively useless for recording the structure of the larger and thicker particles; moreover, the necessity for careful observation when filling in the details cannot be overrated; the method is more tedious than the photographic, but it is of greater value.

It frequently happens that starch or fixed oil may be present in inconveniently large proportions, as is the case with many rhizomes, roots, cereals, oil-seeds, etc. Oil is removed by washing with ether-alcohol. Starch is removed by boiling with water acidified with hydrochloric acid, centrifuging, washing with water, and mounting in a solution of chloral hydrate; the latter is usually necessary as the deposit is often turbid, but clears with the chloral hydrate.

The next step is the identification of the powder. If it has not already been recognised during the examination, then recourse must be had to one of the several identification tables available. Those of Schürhoff and Zörnig are based upon the structure alone; those of Schneider and Kraemer are based primarily on the colour. Zörnig's table has been carefully worked out, but the illustrations in Schneider are useful. If the powder cannot be identified from these, then special works such as Solereder's "Anatomie der Dicotyledonen" may be consulted. No identification

is satisfactory that has not been confirmed by comparison with the genuine powder, and it is therefore essential to have ready to hand a series of the most important. Southall and Barclay issue an excellent collection, but it is very desirable to be in a position to prepare them for oneself. For this purpose the most useful apparatus is a small mechanical mortar; the drugs to be ground are cut into small pieces if necessary, well dried, and then ground and sifted until the whole has passed through a No. 60 or 80 sieve. The powder so obtained should be again dried, and a piece of filter-paper saturated with chloroform introduced into the bottle in which it is to be kept. Without this precaution insect pests are liable to make their appearance and cause trouble.

This method of confirmation is to be preferred to comparison with mounted specimens, which are seldom really normal.

2. *Methods for the Determination of the Purity (and Normality) of a Powder.*— In determining the purity of a powder the smoothed surface is examined as already described, and any fragments that may appear abnormal are removed with a moistened needle for further examination.

Next in the examination of the powder it is necessary to be sure that each particle observed is, or at least might be, derived from the drug in question. This presupposes a knowledge of the structure of the drug, but comparison with a standard powder often suffices, and should never be omitted. Even if this be the case the powder may nevertheless not be normal, and one must be certain, by further comparison again, that the various tissues are present in normal proportion. It is advisable also to compare the amount of cell-contents present with those present in a normal powder.

Care must be taken in pronouncing a powder to be adulterated, because occasional fragments of tissues not present in standard samples have been found. Drug powders are not usually made from selected drugs—thus rhizomes may have buds and stem-portions present; barks may bear on their inner surface strips of wood; leaves may be accompanied by occasional flowers or fruits. The proportions in which these abnormal tissues are present have to be carefully considered.

It might be assumed that with the identification of a simple powder and determination of its purity and normality as indicated, the case for the microscope would be closed, and that this instrument would not afford any further means of judging of the quality. Such, however, is not the case. It is well known that many drugs and spices are liable to be attacked by the larvæ of various beetles, particularly those of *Sitodrepa panicea*, *Lasioderma serricorne*, *Niptus hololeucus*, and *Ptinus tectus*. The larva feeds upon the drug, its excrement collecting often in considerable quantity; it eventually passes into the mature beetle, which then frequently leaves the drug to lay its eggs elsewhere. The powder made from such worm-eaten drugs closely resembles the powder made from sound drugs, yet to sell it as genuine is surely a sale to the prejudice of the purchaser.

As the mature beetle frequently leaves the drug after the mischief has been done, it is necessary to have a means of concentrating the animal remains from a comparatively large quantity of powder by means that allow of the identifica-

tion of those remains by means of the microscope. Taking advantage of the highly resistent nature of the chitinous portions of the beetle the following method was devised:

Five grms. of the powder are extracted with ether in a Soxhlet, the defatted powder dried and boiled with 100 c.c. of 5 per cent. hydrochloric acid for five minutes in a tared flask; 150 c.c. of water are added, the powder allowed to settle, and washed once by decantation. For every 35 grms. of water and powder in the flask 6 c.c. of concentrated sulphuric acid are added, and then after washing are added in small portions, and cooling again if there is any considerable rise in temperature, 10 c.c. of a 1 in 1 aqueous solution of chromic acid. The mixture is allowed to stand with occasional agitation for thirty-six hours or longer. The solid particles are exhausted by centrifuging, washed with water, alcohol, and ether successively, then dried, and mounted in xylol balsam.

The residue thus obtained will usually consist of little else than sand and beetle; it depends chiefly on the amount of sand present in the powder. The particles of beetle are readily detected by their conspicuous colour, and most of them will exhibit either hairs or the scars of hairs.

By this method I have detected the beetle in carefully prepared mixtures containing only 1 part by weight of beetle in 500,000 of powder; as all drugs are not equally favourable for the detection of such minute proportions, too much stress should not be laid on these figures, but they are interesting as showing the extreme delicacy of the microscopical method when carried out under suitable conditions.

3. *Methods for the Determination of the Composition of a Compound Powder.*—The identification of the constituents of a compound powder is, of course, much more difficult than the identification of a simple powder. I usually adopt the following method: The powder is searched under the microscope for any cells, tissues, or cell-contents which appear unusual, and, therefore, characteristic and probably identifiable. It is generally possible to find and identify such. The observer should make himself familiar with the anatomy of these, and again examine the powder, disregarding these tissues and making sketches of the tissues that do not belong to them. These must now be sorted out, those that apparently belong to the same (unknown) drug being grouped together; thus, fragments from a seed, a leaf, a root, may often be sorted out. Search must then be made through the literature at disposal to identify them, if possible. It is a laborious and often thankless procedure, but I know of no other way.

From the examination of vegetable powders for identity, purity, and composition, I pass finally to the detection of such powders under somewhat unusual conditions —viz., in the fæces after their passage through the system. It is quite conceivable that the expert may be called upon to examine human fæces, either for the detection of possible toxic vegetable drugs or for other purposes.

I have found the following method of preparing fæces for microscopical examination satisfactory: The fæces are transferred to a wide-mouthed bottle capable of holding six or eight times their volume. Three or 4 volumes of water are added, and the mixture shaken gently, preferably in a mechanical shaker, until all lumps are

broken up and a uniform cream is produced, adding more water if necessary. About 50 c.c. of this are transferred to a flask, 100 c.c. of ether are added, and the whole shaken thoroughly, but not violently, and the ethereal solution poured off; the same volume of a mixture of equal volumes of ether and alcohol is next added and the whole again shaken. After filtration through paper under diminished pressure the residue is washed with alcohol and returned to the flask, water added, and shaken until evenly diffused, then strained through muslin. The strained liquid is set aside and the residue washed on the muslin until the adhering brownish emulsion has disappeared. It is then transferred to a straight-sided glass dish and washed from the muslin with water. The larger fragments will now be in the dish; the finer in the strained liquid.

The fragments in the dish should be examined with a magnifying-glass, and such as are to be examined removed with a needle and mounted on a slide in dilute glycerol or solution of chloral hydrate.

The strained liquid with the finer particles in suspension may be centrifuged, or, better, allowed to settle for twenty-four hours in a conical glass and the supernatant liquid decanted. Part of the residue is then examined directly under the microscope, while another part is mixed with 2 volumes of solution of chloral hydrate, and, after standing for a short time, centrifuged. In the deposit thus cleared by chloral hydrate the cellular débris is very distinct, while that not so treated retains the cell contents.

I have found this method expeditious and satisfactory. The whole operation may be completed in a morning and the preparations ready for examination in the afternoon without any unpleasant odour being perceptible.

The results obtainable by a thorough and systematic examination of the fæces are extremely interesting, but the complete identification of all the fragments found requires an extensive knowledge of the anatomy of vegetable and animal foods, and not a little patience in the examination of a somewhat voluminous material. In a recent cursory examination I found without difficulty: (1) Currants; (2) raisins: skins and seeds; (3) tomato: skins, seeds, and pulp; (4) meat fibres; (5) oats (pericarp), etc.; (6) rhubarb stem; (7) potato; (8) wheat; (9) mustard; (10) pepper; (11) coffee; (12) beetle. The beetle I was able to identify as the granary beetle, *Niptus hololeucus*, and I presume it was in the oatmeal from which the porridge (oatmeal) had been made.

After taking a small teaspoonful of previously exhausted powdered senna and about the same quantity of powdered liquorice root adulterated with ground almond shells, I found in the strained liquid obtained, as indicated, abundance of almond shells, practically unaltered, the bast-fibres and vessels of liquorice root, now deprived of their otherwise characteristic yellow colour, and the hairs of senna leaves, together with very occasional portions of the epidermis.

While I have thus endeavoured to indicate the methods that I have personally adopted with a fair measure of success, I feel I must add, that success will only come to those who bring neatness of manipulation, intelligence, inclination, and unlimited patience to bear on the problems submitted to them.

Discussion.

The President said those who, like himself, had been connected with the examination of food and drugs since the passing of the Act in 1875 would recollect that in the early days of their work nearly all of it was done with the microscope, following the lines laid down by Dr. Hassall. Then came a period when the microscope was less used, but the practice was again changing, and increasing importance was being attached to microscopical examination. The passing of the Fertilisers and Feeding Stuffs Act, too, compelled resort to the methods taught by Hassall half a century ago and the exposition which Professor Greenish had given of such methods was most welcome.

Mr. T. Macara said that in some recent work on the subject of the detection of agar-agar in jam he had found it very difficult to detect the diatoms in the ordinary way described in the textbooks, by concentrating the fibre after treatment with permanganate and sulphuric acid; but he had found that if the concentration were carried still further by igniting the fibre the diatoms were obtained quite readily.

Mr. E. R. Bolton said that personally he rather preferred photography to sketching, owing to the fact that in sketching one found oneself liable to draw things that one fancied ought to be there but were not. Apart from this, photography was convenient for record purposes, but of course sketching had undoubted advantages if the imagination were kept within due bounds.

Mr. J. F. H. Gilbard remarked that another point in connection with photomicrography was that the photographic plate might register more than was seen by the eye. On the other hand, when working with the microscope without the camera, one could, as Professor Greenish had mentioned, manipulate the fine adjustment in such a manner as to obtain views of several different layers; but this result might also perhaps to some extent be obtained with the camera by reducing the aperture of the lens, say by means of a Davis shutter, which increased the depth of focus, although to some extent the "resolution" of the objective was sacrificed.

Mr. E. T. Brewis observed that Professor Greenish had made no reference to the subject of quantitative work with the microscope. He should like to hear what had been Professor Greenish's experience as to the possibilities of estimating the proportions of a mixture of powders.

The President thought that Professor Greenish had made out a very good case indeed for drawing as against photography, though he must confess that he himself found photo-micrography very fascinating; and, moreover, it took up so little time as compared with sketching that it was now almost a necessity to photograph rather than spend time in drawing.

Professor Greenish said that he was obliged to Mr. Macara for his suggestion with regard to the detection of agar-agar. The question of quantitative work was a very difficult one, and he had purposely avoided reference to it. He only knew of one way in which an approximate estimate of proportions could be made—namely, by making up mixtures as nearly as possible like the powder under examination, comparing them with it under the microscope and making a rough guess. In this way an idea of the proportions could be obtained, but it would only be a very rough approxi-

mation. Professor Meyer had been working at the subject for some time, and one of his own colleagues was investigating a method of estimating the proportions in mixtures of starches the granules of which were of about the same size. It had been shown that by a method of counting some approximate knowledge could be obtained of the proportions in such a mixture, but that was all. He agreed with what had been said as to the advantages of photo-micrography, and thought that a demonstration of its application before the Society would be much appreciated. He considered, however, that the main value of drawing was as a means of cultivating one's own powers of observation. For that purpose any number of drawings might be made, but, supposing these were published, would that have the effect of cultivating other people's powers of observation?

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Comparison of Methods for the Estimation of Casein in Milk. C. B. Hersey. (*J. Ind. and Eng. Chem.*, 1916, **8**, 335-336.)—Three methods were investigated: (1) The A.O.A.C. standard official Kjeldahl-Gunning method; (2) the Van Slyke volumetric method (N.Y. Exp. Sta. Tech. Bull., **10**, 231-241); and (3) the Hart centrifugal method (Wis. Exp. Sta. Bull., **156**, 22). The details of this last-named method were followed as given in the original paper, with the exception that in place of hand power the centrifuge was electrically driven, with rheostat for speed control. It was found that while 75 per cent. of the Hart estimations agreed with the official method to within 0·1 per cent., only 36 per cent. of the Van Slyke estimations fell within these limits. There was also a maximum variation between the Hart and the official methods of 0·54 per cent. casein, while twelve estimations by the Van Slyke method varied over 1 per cent. from the official out of 148 estimations, and one maximum variation occurred of 1·88 per cent. The total time required by the official method is much longer than in either of the other two cases, while the Hart method requires but a small fraction of the time of the others, and has the additional advantage of requiring neither standardised solutions nor final calculation of results. H. F. E. H.

Composition of Embalming Agents Used by the Incas. L. Reutter. (*Comptes rend.*, 1916, **162**, 689.)—Two resinous masses, which had been used by the Incas of South America for embalming their dead, were found to consist of tolu or Peru balsam, mixed with salt, and vegetable matter rich in tannin and essential oils. They were thus of similar composition to the embalming agents of the ancient Egyptians, which were composed of Judæan bitumen, storax, turpentine resins, and sodium carbonate; and to those of the ancient Carthaginians, which consisted of bitumen, storax, turpentine resins, and vegetable matter rich in essential oils and especially in menthol and thymol. C. A. M.

Electrolytic Determination of Bismuth in Bismuth β-Naphthol. B. L. Murray. (*J. Ind. and Eng. Chem.*, 1916, **8**, 257-258.)—The electrolytic process may be applied for the estimation of bismuth after igniting the sample to remove organic matter and dissolving the residue in nitric acid. A portion of 0·3 grm. of the sample is weighed into a porcelain crucible and heated very gently to decompose the β-naphthol; the crucible is finally ignited at full red heat for three minutes to burn off the last traces of carbon.* The residue, which is yellow in colour, consists mainly of bismuth oxide, with a little metallic bismuth. The crucible is placed in a small beaker, and a mixture of 4 c.c. of nitric acid (sp. gr. 1·4) and 5 c.c. of water is added and heated on a steam bath to complete solution. The solution is washed into a mercury cathode cup, which may consist of a 50 c.c. Erlenmeyer flask, and the total volume of liquid should not exceed 20 c.c. Electrolysis is conducted with a maximum current of 4·5 ampères at 6 volts, with an anode rotating at 1,000 revolutions per minute for a period of forty-five minutes. The current is initially applied at 1 ampère and gradually increased to 4·5; some black masses are seen to form, but the high speed of rotation of the anode prevents their accumulation and all disappear. At the end the cathode is washed by siphoning with water while the full strength of current is maintained. The residual solution should be tested for bismuth with hydrogen sulphide. After two or three washings with water, followed by alcohol and then ether, the mercury cathode is weighed, the increase in weight representing the bismuth. J. F. B.

Electroltyic Determination of Mercury in Mercury Oleates. B. L. Murray. (*J. Ind. and Eng. Chem.*, 1916, **8**, 257.)—The following method affords a rapid and accurate separation of mercury from oleates, which in the ordinary way is an extremely tedious operation: About 0·7-1·0 grm. of the oleate is weighed into a mercury cathode cup (*e.g.* a small beaker of 50-75 c.c. capacity); 15-20 c.c. of 10 per cent. hydrochloric acid are added and 15 c.c. of toluene. The cathode cup is placed inside a larger vessel to which water can be added later if it becomes necessary to cool the contents. After attaching the anode and making the connections in the ordinary way, the electrolysis of the heterogeneous mixture is started gradually, slowly increasing the current up to 3 ampères in the course of about ten minutes. The current (3-3·5 ampères at about 8 volts) is then maintained for about thirty minutes, the anode rotating at 800 revolutions per minute. As the electrolysis proceeds the mixture becomes heated nearly to boiling-point. It is essential that the heat developed be sufficient to melt the oleate, but if there is a tendency to boil over, water may be poured into the outer vessel to reduce the temperature not below 60° C. When the mercury is all deposited, the cathode cup is washed out by siphoning in the ordinary way with water, after which the metallic mercury is washed with alcohol, dried by ether, and finally weighed. J. F. B.

Electrolytic Determination of Mercury in Mercury Salicylates. B. L. Murray. (*J. Ind. and Eng. Chem.*, 1916, **8**, 258.)—The following rapid and convenient method gives reliable results with mercury salicylates: About 0·3 grm.

* The danger of losing bismuth during ignition should not be lost sight of.—EDITOR.

of the sample is weighed into a mercury cathode dish and dissolved in 10 c.c. of sodium sulphide solution (sp. gr. about 1·18). To this are added 20 c.c. of 10 per cent. potassium hydroxide solution. The mixture is electrolysed with a current of 1 ampère at 7 volts until the mercury is completely deposited, usually for about thirty minutes. The anode should rotate at about 500 revolutions per minute. After the electrolysis the liquid is decanted off, the mercury washed with water until free from alkali, then with alcohol, followed by ether, and finally weighed. J. F. B.

Qualitative Tests for Gum Arabic and its Quantitative Estimation. C. E. Waters and J. B. Tuttle. (*J. Ind. and Eng. Chem.*, 1916, **8**, 413-416.)—A number of qualitative tests for gum arabic have been examined, the most characteristic of which is the precipitate formed with basic lead acetate; this is of a peculiar curdy consistence, like a white jelly, quite different from the slight precipitates given by dextrin and gum ghatti. Other useful tests are a mixture of copper sulphate and sodium hydroxide, which gives a blue precipitate and colourless supernatant liquor with gum arabic, and a mixture of neutral ferric chloride and alcohol. The authors have worked out a method for the estimation of gum arabic by precipitation with ammoniacal copper acetate and alcohol. The reagent is made with 50 grms. of copper acetate dissolved in water with an excess of ammonia and diluted to 1 litre, using water and alcohol in such proportions that the final solution contains 50 per cent. of alcohol. For each estimation, 50 c.c. of gum arabic solution, representing 0·25 grm. of gum, are mixed with an equal volume of alcohol and 25 c.c. of the copper solution added while stirring. The precipitate is allowed to settle, collected on a tared paper, washed with 50 per cent. alcohol containing ammonia, then with 75 per cent. and lastly with 95 per cent. alcohol. It is dried at 105° C. to constant weight and then incinerated. The amount of ash is deducted from the dry weight and the difference called "net gum arabic." An allowance is made for the moisture required to express the result as air-dry gum. This may be determined by drying some of the original gum at 105° C. in a current of hydrogen. The mineral constituents of the original gum may be neglected. The method gives fairly satisfactory results, but has not been fully studied in relation to mixtures of different gums; there are indications that dextrin and gum ghatti tend to be carried down with the gum arabic. J. F. B.

Investigations on Fruit Jellies. W. V. Cruess and J. B. McNair. (*J. Ind. and Eng. Chem.*, 1916, **8**, 417-421.)—To be suitable for jelly-making the fruit must contain a large supply of pectin and acid, or if not pectin ready formed, a large supply of compounds which break down into pectin at the temperature of boiling water. Deficiency of acid may be made up by the addition of citric acid or lemon juice. As a general rule, the sliced fruit is covered with water and boiled slowly until tender, the juice is strained off and tested for Brix degree and acidity; if more dilute than the original fresh juice it is concentrated; sugar is then added at the rate of 1·25 part by volume to 1 of juice. The mixture is boiled down until its boiling-point is 104°-105° C., equivalent to a concentration of 65-70 per cent. of dissolved solids. Under these conditions, among the Californian fruits, grapes, apples, loganberries, blackberries,

lemons, and pomelos contain sufficient quantities of both pectin and acid to give good jellies. Oranges contain sufficient pectin, but are deficient in acid; when mixed with lemons at the rate of 2 : 1 much better jellies are obtained. Apricots and cherries occasionally give jellies, but are generally deficient in pectin. Pomegranates and strawberries do not contain sufficient pectin, although the acidity is sufficient. Peaches, pears, and huckleberries are deficient both in pectin and acid. Figs and citron-melon give satisfactory jellies when acidified with lemon juice. An acidity between 0·5 and 1·5 per cent. expressed as citric acid in the fruit juice represents the optimum range for jelly making. A sugar density of 65° Brix is necessary to prevent damage by moulds. With densities above 70° Brix there is danger of crystallising unless glucose is used; jellies made from fruits of low acidity are the most liable to crystallise. Clarification of the juices is materially assisted by the addition of 1-2 kilos. of Spanish clay per hectolitre of juice, the clay being previously made into a 10-20 per cent. suspension in water. Addition of clay is followed by heating to 100° C. and allowing to settle. The ordinary household method of making jellies, with prolonged boiling, leads to loss and modification of fruit flavours. Far better results are produced by expressing the juice from crushed fruits rich in pectin, adding sufficient sugar to bring the density up to 65° Brix and heating to dissolve the sugar.

J. F. B.

Analysis of Non-Alcoholic Lemon and Orange Extracts. E. L. Redfern. (*J. Ind. and Eng. Chem.*, 1916, **8**, 421.)—Flavouring extracts have recently appeared containing no alcohol, in which the essential oils are held in suspension by a mixture of gum tragacanth and glycerol. These extracts cannot be assayed by the ordinary methods without some preparation. They are quite viscous when cold, but on warming can be measured in an accurately graduated measuring cylinder; the use of a pipette is unsatisfactory, as the liquid adheres to the walls, whereas a graduated cylinder may be drained into a flask, and afterwards rinsed out with alcohol. For the analysis of such extracts, 25 c.c. are measured out, transferred to a flask, and shaken with 25 c.c. of 95 per cent. alcohol. The mixture is filtered on a Gooch crucible, and the alcoholic extract collected in a 100 c.c. graduated flask, care being taken to prevent any of the precipitated gum from running into the crucible. The precipitate is washed several times with 95 per cent. alcohol, and the filtrate made up to 100 c.c. The precipitation method, using 50 c.c. of this solution, does not give good results, as, owing to the high percentage of alcohol, a large portion of the oil remains in solution. The method suggested by Howard (ANALYST, 1908, **33**, 236), however, is quite satisfactory, showing 4·96 and 5 per cent. in duplicate tests on a 5 per cent. standard lemon oil extract, and 4·8 per cent. on an orange oil extract. In these tests a Babcock milk bottle graduated to 1 per cent. may be used, as the quantity of oil is small; or, better, especially in the case of extracts below standard, a skim milk bottle graduated to 0·01 per cent. is employed. The supernatant liquid in the skim milk bottle can be drawn off by attaching a suction tube to the filling tube on the bottle, and decanting off the remaining small amount through the capillary tube, as the chloroform carries the oil present and remains at the bottom.

J. F. B.

Analysis of Maple Products. V. J. F. Snell. (*J. Ind. and Eng. Chem.*, 1915, **8**, 144-148.)—The following are some of the results obtained in the course of experiments designed with a view to detecting adulteration of maple sugar products: Silver nitrate added to maple syrup gives a white precipitate which darkens on standing; the precipitation of silver continues for a period of several hours. Mercuric acetate added to maple syrup produces a light yellow precipitate, while alcohol produces a precipitate containing most of the calcium and potassium. The lead precipitates obtained by the Canadian method (ANALYST, 1914, **39**, 85; *J. Ind. and Eng. Chem.*, 1914, **6**, 216) from six syrups showed a lead content of 66·95 to 69·62 per cent.; average, 68·42. The precipitate from a composite of fifty-four syrups contained 69·41 per cent. of lead, while that from another mixed syrup contained 70·11 per cent. Titration of maple syrup with $\frac{N}{50}$ silver nitrate, (*a*) directly, using electrical resistance measurements to detect the end-point, (*b*) after treatment with basic lead acetate or alumina cream, using potassium chromate as indicator, yielded irregular results. Titration with uranyl acetate gave no useful results. Titration with basic lead acetate solutions, using electrical resistance as indicator, resulted in a useful method of testing the syrup for purity, which will be described in the next paper of the series. A complete analysis of the ash of a mixture of about sixty genuine syrups showed more chlorine and less phosphoric acid than the analyses previously recorded (*cf.* ANALYST, 1913, **38**, 499; 1914, **39**, 85).

H. F. E. H.

Analysis of Maple Products. VI. Volumetric Basic Lead Acetate Test for Purity of Maple Syrups. J. F. Snell, N. C. MacFarlane, and G. J. van Zoeren. (*J. Ind. and Eng. Chem.*, 1916, **8**, 241-243.)—The fact that basic lead acetate produces a heavy precipitate in genuine maple syrups is used as a volumetric test for the detection of adulteration, the end-point being determined by the electrical conductivity of the mixture. The basic lead acetate solution is prepared from a cold-saturated solution, diluted, filtered, and made up with the hydrometer to a sp. gr. of 1·033. It must be kept in a bottle connected with a burette, and protected from carbon dioxide. The syrup to be tested is diluted with water, boiled until the temperature reaches 104° C., filtered through cotton wool, and cooled. Ten c.c. are diluted to 100 c.c., and 60 c.c. of the solution taken for the test. The electrical resistance is measured, using a dip electrode, then 1 c.c. of lead solution is added from the burette, the mixture stirred well, and the resistance again determined. The temperature must be kept constant over the whole series of experiments. The measurement of the resistance is repeated after the further addition of lead solution, 1 c.c. at a time, until 10 c.c. have been added. The resistances found are plotted as a curve against the number of c.c. of basic lead acetate corresponding to them. If the syrup is genuine, the graphic results take the form of two intersecting straight lines, the point of intersection being the value recorded; with genuine syrups this point falls between the limits of 4·8 and 6·6 c.c. As the majority of adulterated samples gave either continuous curves or break-points lying outside the limits mentioned for pure maple syrups, it is concluded that the method is capable of giving useful indications as a rapid approximate test; a few exceptions were, however, noted.

J. F. B.

Analysis of Maple Products. VIII. Application of the Conductivity and Volumetric Basic Lead Acetate Tests to Maple Sugar. J. F. Snell and G. J. van Zoeren. (*J. Ind. and Eng. Chem.*, 1916, **8**, 421-422.)—Maple sugars prepared from pure maple sugars already investigated were dissolved again to form syrups, and tested according to the methods described for the conductivity and volumetric basic lead acetate tests (see preceding abstract). It was confirmed that the values found for the sugars came accurately within the limits found with the genuine syrups. The method prescribed consists in dissolving a fairly large representative sample of the sugar (*e.g.*, 100 grms.) in hot water, boiling down the solution to a boiling-point of 103·9° C., filtering through cotton wool, and testing the resulting syrup as directed in Papers VI. and VII. (see preceding abstract).

J. F. B.

Estimation of Nicotine in Tobacco and Tobacco Extracts. A Critical Examination of Methods. H. B. Rasmussen. (*Zeitsch. anal. Chem.*, 1916, **55**, 81-131.)—A method described by Bertrand and Javillier (ANALYST, 1909, **34**, 219) was found to yield accurate results; the method depends on the precipitation of the nicotine by means of silicotungstic acid, and the following procedure, introducing slight modifications of the original method, is recommended for the estimation of nicotine in tobacco and in tobacco extracts. Ten grms. of the dry powdered tobacco are treated in a flask with a mixture of 3 parts of 33 per cent. sodium hydroxide solution and 1 part of alcohol; 50 c.c. of ether and 50 c.c. of petroleum spirit are then added, the flask is closed with a stopper, and the mixture shaken at intervals for five hours. The liquid portion is now passed through a covered filter, 50 c.c. of the filtrate are shaken with 25 c.c. of 1 per cent. hydrochloric acid, the aqueous acid layer is separated and mixed with about 10 c.c. of 12 per cent. silicotungstic acid solution. After ten hours the precipitate is collected on a weighed filter, washed with 1 per cent. hydrochloric acid, dried at 120° C., and weighed. The weight of the precipitate is multiplied by 0·0102 to obtain the quantity of nicotine. Alternatively, the precipitate may be ignited together with the filter in a platinum crucible and the residue weighed; its weight multiplied by 0·1140 gives the quantity of nicotine in the precipitate. In the case of tobacco extract, 4 grms. of the sample are treated with 5 c.c. of 33 per cent. sodium hydroxide solution, and 5 c.c. of water, 25 c.c. of ether, and 25 c.c. of petroleum spirit are added. The mixture is shaken occasionally during five hours, then filtered, and the filtrate treated as described. The presence of ammonia does not interfere with the method, but pyridine causes the results to be too high, especially if it is present in relatively large amount. Distillation with steam from an acetic acid solution seems to afford the best means of separating pyridine from nicotine; the pyridine distils over, whilst the nicotine remains in the acid solution. Of other methods investigated, that described by Kissling and Koenig's polarimetric method (*Chem. Zeit.*, 1911, **35**, 521) were found to be reliable; Keller's method (ANALYST, 1898, **23**, 235), and Toth's method (*ibid.*, 1902, **27**, 12) gave less accurate results, and Ulex's method (*ibid.*, 1911, **36**, 143) was untrustworthy. A method proposed by Degrazia (*ibid.*, 1911, **36**, 280) yielded low results, owing to the incomplete distillations of the nicotine under the conditions

prescribed. In the case of Thoms' method, it was found that the nicotine was liable to be contaminated by other substances which are also precipitated by the potassium-bismuth iodide reagent employed. (See also Schroeder, ANALYST, 1911, **36**, 106; Chapin, *ibid.*, 1911, **36**, 544.) W. P. S.

Estimation of Stearic Acid in Butter Fat. E. B. Holland, J. C. Reed and J. P. Buckley, Jr. (*J. Agric. Research*, 1916, **6**, 101-113.)—From an experimental study of Hehner and Mitchell's method of estimating stearic acid (ANALYST, 1896, **21**, 316) the authors find that the amount of stearic acid contained in a saturated alcoholic solution varies with the quantity present before cooling, and they conclude that supersaturation probably occurs as a result of insufficient stearic acid. Alcoholic solutions containing 0·4 to 0·5 grm. of stearic acid per 150 c.c. yield crystals readily, and when applied to the insoluble fatty acids of butter give an additional deposit of stearic acid (mol. weight = 284·64). Concordant results are obtained provided the details of the method are observed: About 0·5 grm. of the melted insoluble fatty acids is treated with 150 c.c. of a solution of 3 grms. of stearic acid in 1,000 c.c. of 95 per cent. alcohol, which is measured with a pipette at 30° C. The cylindrical bottle ($2 \times 6\frac{3}{4}$ inches) is closed with a rubber stopper, shaken at a gradually increasing temperature until a clear solution is obtained, and then placed in a wire pocket in an ice-tank through which a current of water is continually pumped. This insures the temperature being kept constant at 0·1° C. The following morning the solution liquid is gently shaken, by inverting the bottle several times, and then drawn off through an inverted thistle funnel containing cotton wool as a filter. Simultaneously a blank estimation is made with the alcohol-stearic acid solution containing an additional quantity of stearic acid equivalent to that expected from the fatty acids under examination. By deducting the additional stearic acid from the weight recovered the deposit in the true blank is obtained. The deposits are dissolved in ether, the solvent evaporated in a wide-mouthed flask, and the residue dried at 100° C. Lauric, myristic and oleic acids in relatively large quantities had no appreciable influence on the results, but palmitic acid increased the solubility of the stearic acid and affected the crystalline structure of the precipitate. The addition of palmitic acid to the insoluble fatty acids of butter fat reduced the amount of deposit, but by increasing the relative amount of stearic acid the solvent action of palmitic acid could be counteracted to a large extent. With butters containing an average amount of palmitic acid a solution containing up to 3·4 to 3·7 grms. per litre was the most reliable, but the necessary proportion varied with the nature of the alcohol. The insoluble fatty acids of butter fat thus examined yielded from 7 to 22 per cent. of stearic acid (mol. weight of several precipitates 284·38). The amounts appeared to be influenced by the food of the animal. Cows fed with beef tallow gave butter with fatty acids containing 15·2 to 17·56 per cent. of stearic acid, while the amounts from cows fed with palm oil were 13·8 to 14·9 per cent., and those from cows fed with material poor in fat averaged 8·70 per cent. The amount of stearic acid thus separated from the insoluble fatty acids of palm oil was 8·91 per cent., which was considerably higher than the recorded amounts. C. A. M.

Proteins of Wheat Flour and their Relation to Baking Strength. **M. J. Blish.** (*J. Ind. and Eng. Chem.*, 1916, **8**, 138-144.)—After an historical survey embracing the work of Osborne (*Amer. Chem. J.*, 1893, **15**, 392-471; 1894, **16**, 524-535); Snyder and Chamberlain (*J. Amer. Chem. Soc.*, 1906, **28**, 1657-1667); Wood (ANALYST, 1907, **32**, 119-293); Shutt; Baker; and Hulton (ANALYST, 1908, **33**, 322); Ford and Guthrie (ANALYST, 1908, **33**, 323) and other workers, the author proceeds to discuss the nature of the nitrogen distribution in wheat proteins of strong and weak flours as determined by the Van Slyke method. The individual proteins of strong and weak flours were found to be identical in chemical composition—a finding confirmed by Gróh and Friedl (*Biochem. Zeitsch.*, 1914, **66**, 154). The ratio of gliadin to glutenin is much more nearly constant in flours of different baking values than has hitherto been supposed, but there is a greater variation in the percentages of the so-called "soluble proteins" (albumin and globulin). Since the various proteins in the same flour differ widely in their content of ammonia nitrogen, the estimation of ammonia nitrogen in flours, in extracts of flours made with various solvents, and in the crude gluten of flours after their previous complete hydrolysis with strong mineral acid, can be made to serve as an accurate indication of the amounts of the various proteins present, since the proteins of widely different flours have been shown to have the same chemical constitution.

The following table shows the distribution of nitrogen in the proteins of typical strong and weak flours:

Units Determined.	1. In the Gliadin. Van Slyke's Method. Per Cent. of Total N.		2. In the Glutenin. Van Slyke's Method. Per Cent. of Total N.		3. In Crude Glutens. Per Cent. of Total N.		
	Strong.	Weak.	Strong.	Weak.	Strong.	Weak.	Weak.
Nitrogen as—							
Ammonia	23·13	25·90	16·50	16·17	22·87	23·19	23·69
Humin	0·50	0·57	1·84	1·66	1·19	1·37	1·11
Cystine	0·37	0·29	0·18	0·18	0·46	0·70	0·43
Arginine	4·55	4·47	9·69	9·27	5·24	5·54	5·54
Histidine	6·77	5·62	5·47	7·59	2·79	1·28	1·50
Lysine	0·65	0·97	2·61	1·90	2·21	2·60	2·28
In Filtrate from Bases:							
Amino bases ...	53·46	54·10	53·59	53·38	55·21	56·15	55·14
Non-Amino bases ...	7·44	7·55	9·52	9·35	9·54	9·88	10·13
	99·97	99·47	99·40	99·50	99·51	100·71	99·82

H. F. E. H.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Effect of Pasteurisation on Mould Spores. **C. Thom and S. H. Ayers.** (*J. Agric. Research*, 1916, **6**, 153-166.)—Studies were made with spores from pure cultures of a series of moulds, including over forty species of *Penicillium*, a large number of *Aspergillus* and of the *mucors*, and, in some experiments, *Oidium lactis*

and one species of *Fusarium*. It was found that the "bulk" process of Pasteurisation in which milk was heated to 62·8° C., and maintained at that temperature for thirty minutes, killed the conidia of every species investigated, except those of *Aspergillus repens*, *A. flavus*, and *A. fumigatus*. The moulds which survive are found only occasionally in milk. The "flash" process of Pasteurisation in which milk was heated to 73·9° C. for a period of thirty seconds destroyed the spores of all the moulds tested, with the exception of many spores of one form and occasional spores of three more forms. At 79·5° C. only occasional spores of two forms developed. When the heating process was performed in dry air for a period of thirty seconds at 93·3° C., 31 out of 42 forms of *Penicillium* and 7 out of 24 forms of *Aspergillus* were destroyed, but none of the cultures of *mucors*. A temperature of 121·1° C. over a period of thirty minutes killed all the forms of *Penicillium* spores tried, but left an occasional living spore in one species of *Aspergillus* and 3 out of 6 *mucors*. Careful study of the cultures showed that the first effect of heating was to delay germination. It was found that there was frequently a survival of a few spores where a majority of the spores die; there may be therefore a difference of as much as 11° C. between the temperature at which an occasional culture is completely killed, and that at which cultures of that species are uniformly killed. These results resemble those obtained in determining the thermal death-point of bacteria. The results obtained were studied in an attempt to correlate heat resistance with size of spore or thickness of spore wall, but no such correlation was found.

H. F. E. H.

Potash in Banana Stalks and Skins. R. H. Ellis. (*J. Soc. Chem. Ind.*, 1916, **35**, 456-457; 521.)—Analyses of banana stalks and skins yielded the following results:

	Stalks.	Skins.
	Per Cent.	Per Cent.
Moisture	91·60	88·20
Dry substance	8·40	11·80
Ash	2·40	1·77
Potash (K_2O)	1·14	1·05
,, in dry substance	13·73	9·03
,, in ash	45·90	57·16

Thus, 1 ton of banana stalks would give 188 lbs. of dry substance containing 13·7 per cent. of potash, or 54 lbs. of ash containing 45·9 per cent. of potash; 16,000 tons of stalks are imported per annum. The quantity of bananas imported per annum into this country would yield upwards of 60,000 tons of skins, or 7,112 tons of dry substance containing 9 per cent. of potash. W. P. S.

ORGANIC ANALYSIS.

Estimation of Alcohol in the Presence of Phenol. J. Ehrlich. (*J. Ind. and Eng. Chem.*, 1916, **8**, 240-241.)—When separating alcohol from phenol by distillation from a strongly alkaline solution, the results are by no means exact, owing to the dissociation of the phenate and the appearance of phenol in the alcoholic distillate. This difficulty may be surmounted by converting the phenol into tribromophenol before distilling. A preliminary separation by distillation from alkali is preferable, except when the proportion of phenol is small. The full method is as follows: 50 c.c. of the sample are measured into a 300 c.c. flask containing 30 c.c. of water and made strongly alkaline with sodium hydroxide to a total volume of about 100 c.c. The liquid is distilled into a 50 c.c. graduated flask containing 1 or 2 c.c. of water, the end of the condenser being extended so that it almost touches the level of liquid in the receiver. When nearly 50 c.c. of distillate have been collected the contents of the receiver are made up to the mark, shaken, and 25 c.c. measured out into another 300 c.c. flask containing 30 c.c. of water. The phenol is precipitated by adding bromine water drop by drop to slight excess, and the liquid immediately decolorised by a few drops of $\frac{N}{1}$ thiosulphate solution. Sufficient strong sodium hydroxide is then added to dissolve the tribromophenol and leave a decided excess of alkali. The full volume should be less than 100 c.c. The liquid is distilled as before, and the contents of the receiver are made up to 50 c.c. The percentage of alcohol calculated from the specific gravity of the distillate $\times 2$ gives the percentage in the original sample. The method is found to be perfectly accurate, the action of the small excess of bromine on the ethyl alcohol being quite inappreciable in a short time at the ordinary temperature. J. F. B.

"Formolite" Reaction of Nastukoff as Applied to Oil Residuals and Natural Asphalts. C. Richardson. (*J. Ind. and Eng. Chem.*, 1916, **8**, 319-321.)—Nastukoff (*J. Soc. Chem. Ind.*, 1904, **23**, 1082) investigated the results of the reaction between petroleum lubricating oils and formaldehyde and sulphuric acid, and determined the percentage of the resulting product, "formolite," obtained from oils of various origin. The author has extended the method to the examination of the heavier, more viscous and solid native bitumens employed in the construction of asphalt pavements, water-proofing, etc. It was found upon applying the method to a heavy liquid petroleum residual of sp. gr. 0·962 that the vigorous action of the acid carbonised the material, so that no further action by the formalin was possible. No satisfactory method being found of obviating this and other difficulties in the use of the method, it was decided to collect and weigh the residual oil which was unacted upon. Six bituminous materials representing distinct types of asphalt and oil residuals of nearly the same consistency were investigated, and it was found that the more thoroughly asphaltic a bitumen is the smaller is the amount of saturated hydrocarbons it contains, as evidenced by the residue left by the treatment of the total bitumen, not only with sulphuric acid and paraformaldehyde, but likewise with fuming and even concentrated sulphuric acid. The use of formaldehyde was there-

fore discontinued, since the materials examined may be as well differentiated by the use of sulphuric acid as by the "formolite" reaction.

	Naphtha-soluble Bitumen (Pure Basis).	Per Cent. Saturated Hydrocarbons by—		
		Ordinary H_2SO_4.	Fuming H_2SO_4.	H_2SO_4 and $(HCOH)_3$.
Texas residual	64·3	44·5	37·5	35·8
California residual	65·0	40·1	38·2	33·0
Mexican ,, ...	72·2	37·5	31·3	25·2
Trinidad ,, ...	73·1	32·7	28·4	24·0
Bermudez refined asphalt ...	71·9	28·3	22·6	21·1
Trinidad ,, ,, ...	64·9	23·7	22·3	22·7

H. F. E. H.

Determination of the Specific Gravity of Fixed Oils in the Tropics. C. H. Wright. (*J. Soc. Chem. Ind.*, 1916, **35**, 457-458.)—In countries where the dew point of the air is above 15·5° C. it is difficult to determine the sp. gr. of a liquid at this temperature owing to the condensation of moisture on the bottle or Sprengel tube. If the oil is cooled to 15·5° C. and its sp. gr. determined by the Westphal balance a similar difficulty arises, since moisture condenses on the surface of the oil and on the platinum wire attached to the plumet. The following procedure is therefore recommended. The weight of water held by a sp. gr. bottle is determined at the temperature of the air; the weight of oil held by the bottle is also determined at the same temperature. The weight of water held by the bottle at 15·5° C. is

$$\frac{W_t \times d_{15\cdot5}}{d_t[1+(t-15\cdot5)a]} \text{ grms.},$$

where W_t = weight in air of water held by the bottle at $t°$ C.; d_t = weight in air of 1 c.c. of water at $t°$ C. (see Sutton's "Volumetric Analysis," tenth edition, 1911, p. 26); $d_{15\cdot5}$ = weight in air of 1 c.c. of water at 15·5° C. (0·99804 grm.); and a = the coefficient of cubical expansion of glass (0·0000258). The weight of oil held by the bottle at $t°$ C. is now divided by the weight of water held by the same bottle at 15·5° C. to obtain the sp. gr. of the oil at $t°$ C. (S_t), and from this value the sp. gr. of the oil at 15·5° C. ($S_{15\cdot5}$) is found from the equation,

$$S_{15\cdot5} = S_t \times \frac{1-0\cdot0007\times15\cdot5}{1-0\cdot0007t} = S_t \times \frac{0\cdot98915}{1-0\cdot0007t},$$

in which the modulus of expansion of fixed oils is taken to be 0·0007 (see ANALYST, 1907, **32**, 295). W. P. S.

Method of Estimating the Amount of Seasoning of Teak Wood. A. C. Sircar. (*J. Soc. Chem. Ind.*, 1916, **35**, 452-454.)—The method proposed depends on the fact that teak wood sawdust yields on steam distillation either

a crystalline or an oily substance, or a mixture of the two, according as the wood is seasoned, unseasoned, or partially seasoned. The oily substance may be separated from the crystalline substance by means of methyl alcohol, in which solvent the crystalline substance is only slightly soluble, and the quantity of oily substance obtained on evaporating the methyl alcohol solution affords an indication of the degree of seasoning which the wood has undergone. One hundred grms. of the freshly-made sawdust from the sample of wood should be steam distilled until 1 litre of distillate has been collected; the distillate is then extracted with ether, the ethereal solution evaporated at ordinary temperature, and the residue weighed. The residue is now treated with 1·5 c.c. of methyl alcohol, which at once dissolves the oily substance, the solution is filtered through a very small filter, the filter washed with a drop or two of methyl alcohol, the alcoholic filtrate is evaporated at ordinary temperature, and the oily residue weighed. The crystalline substance does not come over completely with the first litre of distillate, the succeeding fractions of 1 litre each up to the tenth containing small and practically equal quantities of the substance; even in the case of fresh teak wood, the greater part of the oily substance appears in the first litre of distillate, and none is found in the fourth or fifth litre. When 1 litre of distillate is collected, as prescribed, the weight of the residue soluble in methyl alcohol never exceeds 0·0188 grm. in the case of properly seasoned woods (*e.g.*, woods over 5 years old), and is less than 40 per cent. of the total ether soluble residue obtained from the distillate. Unseasoned woods yield from 0·2 to 0·8 grm. of residue soluble in methyl alcohol, and the residue has a distinct oily appearance; it constitutes from 70 to 80 per cent. of the total ether soluble residue.

W. P. S.

Estimation of Soluble Nitrocellulose in Guncotton. H. C. Mallinson. (*J. Ind. and Eng. Chem.*, 1916, **8**, 401-402.)—According to the British Government specification method the guncotton is treated with ether-alcohol, shaken every fifteen minutes for about six hours, and an aliquot portion of the extract evaporated and dried. The method tends to give high results owing to occlusion of the solvent which is not completely driven off in the drying. It is preferable, therefore, to precipitate the soluble nitrocellulose by pouring the solution into water and to collect and dry the precipitate. The shaking of the guncotton with ether-alcohol is performed far more conveniently by mechanical means. According to the rapid method proposed, 5 grms. of the sample (or less if the degree of solubility is high) are treated with 200 c.c. of ether-alcohol in a graduated 200 c.c. cylinder. Agitation is effected by attaching the cylinder to a block of wood clamped on a shaft revolving at from 5 to 11 revolutions per minute. Complete extraction of the soluble matter is thus attained within one hour, as compared with six hours by hand. After the residue has settled, 50 c.c. of the clear extract are transferred to a dish, and about 500 c.c. of water at 75° to 80° C. are poured slowly down the inside of the dish, the complete evaporation of the solvent being effected by immersing the floating cake of precipitate below the surface of the hot water by means of a rod. The mode of collecting the precipitate depends on its character. If it takes the form of a coherent mass, with only a few detached particles which can be picked out with

the forceps, it is placed between filter papers, after moistening with alcohol and pressed. Drying can then be completed in twenty minutes in the oven at 72° C. If the precipitate takes the form of disconnected flakes it is collected on a pair of counterpoised filter papers, the contents of the dish being washed down with alcohol. The collected matter on the filter is pressed between the folds of a towel, dried in the oven, and weighed with one filter paper in each pan. If preferred, the precipitate may be collected in a Gooch crucible, so manipulated that the precipitate itself makes its own filter-bed. The results are always slightly lower than by the evaporation method, and, therefore, more accurate; the error of the latter, due to enclosed solvent, increases with the quantity of soluble matter. J. F. B.

Direct Estimation of Rubber in a Compound. R. W. Belfit. (*J. Ind. and Eng. Chem.*, 1916, **8**, 326-327.)—The method described gives excellent results with high-grade mixings, but is not applicable to mixings containing lampblack, shoddy, ground leather, starch, egg albumen, or other organic compounds insoluble in acetone, water, or dilute hydrochloric acid. It depends on extraction of the sample first with acetone and then with dilute hydrochloric acid, and the combustion of the residue, the resulting carbon dioxide being absorbed by potash and weighed.

The sample (2 grms.) should pass a 20-mesh sieve, but should not be much finer. It is extracted with boiling acetone for 5 hours, dried in a current of carbon dioxide at 100° C., and weighed. About half of the extracted sample is weighed into a 250 c.c. flask and boiled for thirty minutes with 150 c.c. of dilute (1 : 5) hydrochloric acid. The acid liquid is decanted through an alundum crucible with the aid of suction, and the residue washed three times by decantation and ten times on the filter with water at 60° C. The residue is then dried at 100° C. for three hours in a current of carbon dioxide. After weighing, a portion of about 0·3 grm. is submitted to combustion analysis. No copper spiral is used, but oxides of nitrogen are absorbed together with water by a small quantity of concentrated sulphuric acid containing chromic acid in solution. Any acid gases other than carbon dioxide are absorbed by zinc dust in an appropriate apparatus and the carbon dioxide by potash in the usual manner. From the weight of carbon dioxide found that of the corresponding amount of $C_{10}H_{16}$ is calculated. When fine Para gum is submitted to analysis in this way, about 96% of $(C_{10}H_{16})_n$ is indicated. In the analysis of mixings, therefore, the apparent weight of $(C_{10}H_{16})_n$ in the portion taken for combustion is divided by 0·96 to obtain the corresponding weight of rubber. The percentage of rubber in the original sample is then calculated by reference to the percentage loss on treatment with acetone, the fraction of the original sample taken for the acid extraction and the fraction of the fully extracted sample taken for combustion. G. C. J.

Estimation of Barium Carbonate and Barium Sulphate in Vulcanised Rubber Goods. J. B. Tuttle. (*J. Ind. and Eng. Chem.*, 1916, **8**, 324-326.)—Many specifications now permit the use of barium sulphate without having the sulphur which it contains count as part of the specified total sulphur. The estimation of total barium presents no difficulty (*India Rubber World*, 1914, **51**, 128; U.S. Bureau of Standards *Circular*, No. 38, 3rd ed., 1915, 68), and, if no compound of barium

other than the sulphate is present in the mixing, the necessary correction is readily made. Barium carbonate, however, may be present, and it is therefore necessary to have a means of estimating this. Since lead sulphate may be simultaneously present, the separation of barium carbonate from barium sulphate cannot be carried out by solution of the carbonate in acids, for lead sulphate will pass into solution and subsequently react with the barium with precipitation of barium sulphate. Solution of the lead sulphate in ammonium acetate is also untrustworthy. The following method has proved satisfactory: The rubber (1 grm.) is ignited in an atmosphere of carbon dioxide, the residue finely ground, treated with 5 to 10 grms. ammonium carbonate, 15 to 20 c.c. of strong ammonia, and about 50 c.c. of water, and boiled for fifteen to thirty minutes. This treatment converts lead sulphate into carbonate, but has an almost negligible effect on barium sulphate. The soluble sulphates are removed by filtration and the residue on the filter is washed back into the original beaker and boiled with about 100 c.c. of 10 per cent. acetic acid. The solution is filtered from the barium sulphate, using the same filter as before. In the filtrate, lead is precipitated as sulphide, which is filtered off. Finally, in the filtrate from the lead, the barium originally present as carbonate is precipitated by adding 10 c.c. of 10 per cent. sulphuric acid to the hot solution, allowing to stand in a warm place overnight, filtering, igniting, and weighing as sulphate. G. C. J.

Estimation of Tartaric Acid. B. G. Hartmann, J. R. Eoff, and M. J. Ingle. (*J. Ind. and Eng. Chem.*, 1916, **8**, 422-425.)—The Halenke and Möslinger method for precipitating acid potassium tartrate (*Zeitsch. anal. Chem.*, 1895, **34**, 279) has been taken as the basis of the present work, but, as originally devised, it has been found unreliable when employed on wines and fruit juices containing much free tartaric acid. This is attributed to the reversibility of the main reaction under the influence of the hydrochloric acid liberated, and the difficulty may be surmounted by adding to the wine sufficient alkali to neutralise its acidity, and then the molecular equivalent of pure tartaric acid to convert the neutral tartrates into acid tartrates. In applying the method to wines, 100 c.c. are treated with sufficient $\frac{N}{1}$ sodium hydroxide to neutralise, according to a predetermined titration, and pure powdered tartaric acid equivalent to the alkali used is then added. Subsequently 2 c.c. of glacial acetic acid and 15 grms. of potassium chloride are added, and, when the salt is dissolved, 15 c.c. of 95 per cent. alcohol. The liquid must be stirred until precipitation has started, and is then left overnight at a temperature not exceeding 15° C. The precipitate is collected in a Gooch crucible with pulp filter-bed, using gentle suction, and washed three times with 7 c.c. of a solution composed of 100 c.c. of water, 15 grms. of potassium chloride, and 20 c.c. of 95 per cent. alcohol. The precipitate and filter are transferred to the original beaker with 50 c.c. of hot water, the liquid is brought to the boil and immediately titrated with $\frac{N}{10}$ sodium hydroxide in presence of phenolphthaleïn. The burette reading is increased by 1·5 c.c. to correct for solubility, then multiplied by 0·015, and the quantity of added tartaric acid subtracted. If the liquid during precipitation be stirred mechanically, accurate results can be obtained in thirty minutes. If desired, Rochelle salt may be added instead of tartaric acid, provided its content of tartaric acid be previously determined. In

the case of grape juice, 50 c.c. of the filtered juice are neutralised as described and diluted to 100 c.c. The procedure is then the same as for wines, except that 20 c.c. instead of 15 c.c. of alcohol are used. In the case of syrups, removal of the sugar by fermentation or separation of the acid as lead salt is advisable. In the case of liquids containing tartaric acid, free phosphoric acid, and alcohol, inferior results are obtained, and all the methods become less reliable the older the solutions. This is due to esterification, with the formation of ethyl tartrates. It is found, however, that complete saponification of the esters is produced by adding 5 c.c. of $\frac{N}{1}$ sodium hydroxide to 50 c.c. of the solution in excess of the quantity required to neutralise, bringing to the boil, and allowing to stand overnight. The addition of the calculated amount of tartaric acid, dilution of the solution to 100 c.c., and the continuation of the method as applied to wines yield quantitative results for the total tartaric acid.

J. F. B.

INORGANIC ANALYSIS.

Reduction of Arsenic to the Arsenious State by Cuprous Chloride and Estimation of Arsenic by Distillation as Trichloride. R. C. Roark and C. C. MacDonnell. (*J. Ind. and Eng. Chem.*, 1916, **8**, 327-331.)—In the analysis of arsenical insecticides, the authors obtained very low results when attempting to estimate the arsenic by reduction with ferrous salts followed by distillation as trichloride. Yet this method has often been recommended for the estimation of arsenic, the recommendation being supported by excellent test numbers. A review of the literature, however, discloses the fact that in all these cases of the successful use of the method one or more of the following conditions obtained: (*a*) the arsenic was present in very small amount, (*b*) it was present as element or as arsenite and not as arsenate, (*c*) copper or a copper salt was present.

Cuprous chloride in hydrochloric acid solution effectively reduces arsenic compounds to arsenious chloride, which can then be readily distilled in a current of hydrogen chloride. The sample, containing not more than 0·4 grm. of arsenic, is washed into a distilling flask with 100 c.c. of hydrochloric acid (sp. gr. 1·19), 5 grms. cuprous chloride are added, and the mixture distilled until only about 40 c.c. remain in the flask, when an additional 50 c.c. of acid are added through a tap funnel and distillation continued, this process being repeated until 200 c.c. have been distilled. The distillate is collected in a series of wash-bottles. The first should not contain more than 40 c.c. of water, otherwise a compound of arsenic may separate which cannot readily be redissolved. The adapter from the condenser penetrates the cork of this wash-bottle, but is not sealed in the liquid. A safety tube about twelve inches long penetrates the cork and is sealed in the water. The outlet tube connects to a bend which dips into 100 c.c. of water contained in the second wash-bottle. Both these bottles should be surrounded by ice and water. A third wash-bottle is added as a precaution, but it is unusual for any arsenic to get beyond the second. The distillate and washings from the flasks are nearly neutralised with sodium hydroxide, using phenolpthalëin as indicator, and keeping the solution cool. Sodium bicarbonate is then added in excess, and the solution titrated with iodine solution in the usual manner.

G. C. J.

Estimation of Carbon in Steels and Irons by Direct Combustion in Oxygen at High Temperatures. J. R. Cain and H. E. Cleaves. (*J. Ind. and Eng. Chem.*, 1916, **8**, 321-324.)—The general consensus of opinion seems to be that higher results are obtained with higher combustion temperatures, but this conclusion is rendered doubtful by the fact that the recorded differences are mostly no greater than the unavoidable error of a blank determination, and may quite possibly be due to other causes than temperature, such as variation in size of drillings. Moreover, the published work does not indicate that investigators have always assured themselves that the fluxes and material used to support the drillings were completely free from carbon.

The authors have re-investigated the point and to this end set up rather elaborate apparatus permitting the maintenance of temperatures up to 1500° C. As a result they conclude that the certificates of carbon content sent out with samples by the Bureau of Standards, based as they are on simpler methods of analysis, are not in error by more than 0·015 per cent. (generally *minus*), and that in most cases the error is much less.

In view of this confirmation of the accuracy of simpler methods of direct combustion, the authors do not recommend their elaborate apparatus and somewhat inconvenient method, but these are fully described in the paper, as they may possibly prove useful in the analysis of some special alloys. G. C. J.

Estimation of Carbon in Steel by Eggertz Method. H. Le Chatelier and F. Bogitch. (*Comptes rend.*, 1916, **162**, 709-714.)—Concentrated nitric acid effects more rapid solution of the carbon than does weaker acid, but tends to retard or even prevent complete solution of the iron. The authors, therefore, treat 1 grm. of the borings with 20 c.c. of acid of sp. gr. 1·16, heat rapidly to boiling during one minute, maintain in ebullition another minute, then add 30 c.c. of acid of sp. gr. 1·33 and continue to boil for three minutes longer. After cooling rapidly for one minute, comparison is made with standards in the usual manner. The intensity of the final coloration being dependent on the temperature of digestion, as well as other conditions, the authors prefer to make this digestion at the boiling-point, which is fixed by the acid concentration, rather than to make use of a bath at 80° C. or other temperature, which it is less easy to keep uniform. Experiments are described showing the influence on the final colour intensity of the temperature of digestion, duration of heating, concentration of acid and period of exposure to diffused daylight before the comparison is made, also the necessity for preserving standards from unnecessary exposure to light and for their frequent renewal. The disturbing effect of chlorides in the nitric acid is also demonstrated and the fact that sulphuric acid does not interfere. G. C. J.

New Method of Estimating Fluorine. F. Pisani. (*Comptes rend.*, 1916, **162**, 791-793.)—On adding thorium nitrate to the solution of an alkali fluoride, slightly acidified with acetic or nitric acid, a gelatinous precipitate of thorium fluoride, $ThF_4 + 4H_2O$, is obtained. When dried at 100° C. this loses 1 molecule of water, but for estimating fluorine it is preferable to ignite the precipitate and weigh the

residue of thorium oxide, ThO_2. Too large an excess of the reagent must be avoided, since the precipitate is somewhat soluble in strong thorium nitrate solution. Subject to this precaution the test is capable of detecting 0·01 per cent. of fluorine. In the case of certain insoluble fluorides preliminary fusion with 5 parts of sodium carbonate is necessary, the melt being then taken up with water, and the solution acidified with acetic acid. Hydrofluosilicic acid precipitates thorium in the cold from solutions rendered slightly acid with hydrochloric acid, and is thus a sensitive reagent for thorium even in the presence of cerium, lanthanum, and didymium. Thorium nitrate precipitates hydrofluosilicic acid quantitatively from soluble hydrofluosilicates, while insoluble hydrofluosilicates may first be decomposed by boiling or fusion with sodium carbonate, and separation of the silica by treatment with ammonium carbonate. Hydrofluotantalates and hydrofluoborates are boiled with sodium carbonate solution, the tantalum filtered off, and the filtrate treated with acetic acid and thorium nitrate as described. C. A. M.

Rapid Approximate Assay for Lead. G. Torossian. (*J. Ind. and Eng. Chem.*, 1916, 8, 331.)—An aluminium plate, 5 inches by 2 inches by 0·03 inch, is required. It serves for about 30 estimations. Near each end of the plate a cup-shaped depression is made by laying the plate on the thumb-hole of a crucible tongs and striking with a pestle. The diameter of the cup need not exceed 1 inch, nor its depth $\frac{3}{16}$ inch. Before use, the plate is rubbed with emery-cloth to remove the protective coating of oxide. From 0·15 to 0·2 grm. of the finely-powdered sample is placed in one of the cups, moistened with 1 or 2 drops of dilute (1 : 3) hydrochloric acid, and more acid is added, drop by drop, until the action of the acid on the aluminium is well started. The sample is subjected to this treatment for several seconds, or until the colour of the sample (if coloured) disappears or is notably changed. By this time the sample becomes spongy, may be turned over by a pointed glass rod, or gently stirred and more acid added if necessary. After a minute or two the contents of the cup are stirred with a pointed glass rod for about five minutes, or until all indications point to the completion of the reaction, such indications being the disappearance of the colour of coloured compounds, or the disappearance of the smell of hydrogen sulphide in the case of sulphides. The spongy metallic lead is washed by decantation four or five times until free from acid, and is then pressed together with a glass rod to make it solid and compact, after which a piece of filter-paper is pressed on it to dry it as far as is possible in this way. Finally, 1 drop of water is placed near the cup on the plate, which is then warmed above a small gas flame or lighted match until the water is evaporated. When the water is evaporated, the lead may be assumed to be substantially dry. The dried lead is then detached from the plate and weighed.

The test results with lead oxides, carbonate, sulphate, and acetate are all within 1 per cent. of theory, but there are no test results on naturally occurring minerals, although the author recommends the method as an approximate one for mining engineers and prospectors. G. C. J.

Estimation of Silica. V. Lenher and E. Truog. (*J. Amer. Chem. Soc.*, 1916, 38, 1050-1063.)—Experiments are described which demonstrate the fact that the

failure to recover all the silica in one evaporation is not so much due to insufficient dehydration as to the opportunity afforded by the large mass of silica for its direct solution during the acid treatment. The authors, therefore, do not attempt to carry the dehydration of the first and principal separation of silica anywhere near completion, a course which has the further advantage that the bulk of the silica is less contaminated by bases. Moreover, the first evaporation is carried out as expeditiously as possible to minimise the time during which the acid acts on the bulk of the silica. The residue from the evaporation of the filtrate is more thoroughly dehydrated, but not above 110° C., nor for more than two hours, longer heating showing no advantage, whilst higher temperatures lead to the contamination of the silica by bases, notably by magnesia. The acidified solution of the fusion is evaporated in the usual manner, but evaporation is stopped when the residue begins to powder. The residue is moistened with hydrochloric acid of sp. gr. 1·1, and not with water or concentrated acid, either of which appears to exercise a greater solvent effect. After digestion on the water-bath for ten minutes, 10 c.c. of water are added and filtration proceeded with immediately, the silica being washed with hot 5 per cent. hydrochloric acid. The filtrate is evaporated, the residue dehydrated at 110° C. for two hours, taken up with a little dilute (1 : 1) hydrochloric acid, diluted to 50 c.c. after five minutes digestion on the water-bath and filtered. The silica separated this time is washed with cold 1 per cent. hydrochloric acid.

In silicate fusions, no more sodium carbonate than is necessary should be used, as silica is appreciably soluble in sodium chloride solutions, but many silicates cannot be decomposed with less than 4 parts of sodium carbonate. G. C. J.

Accurate End-Point in Volumetric Estimation of Sulphur in Steel. H. Zschiegner. (*J. Ind. and Eng. Chem.*, 1916, **8**, 324.)—For the titration of hydrogen sulphide with iodine and starch a special titration vessel is used, consisting of a white porcelain beaker, 7 cms. in diameter and 16 cms. deep, to the bottom of which is cemented a thin black disc of hard rubber or celluloid about 2 cms. in diameter. A substitute for this vessel may be made by painting the black spot on the outside of a glass beaker, and then painting the whole of the outside of the beaker with white enamel. The estimation is carried out as usual until the titration is commenced, then the black spot is carefully observed, and, as the solution darkens, the iodine is added more slowly with agitation. Finally, a point is reached when one drop of iodine renders the spot invisible on allowing the solution to come to rest. This is taken as the end-point, and is said to be more easy to work to than the first appearance of a distinct blue colour. The iodine solution is, of course, standardised in a similar manner, using a steel of known sulphur content, an equal volume of hydrochloric acid to decompose the cadmium sulphide, and an equal volume of starch solution. The author prefers a starch solution, prepared by introducing 12 grms. of wheat starch, made into a cream with water, into 2,000 c.c. of boiling water containing 3 grms. of sodium hydroxide. G. C. J.

Estimation of Hardness of Natural Waters, and the Use of Methyl Red as an Indicator. S. A. Kay and S. H. Newlands. (*J. Soc. Chem. Ind.*, 1916,

35, 445-447.)—The methods described are mainly modifications of those described by Hehner (ANALYST, 1883, **8**, 77); the use of methyl red as indicator in the titrations is recommended. Temporary hardness is most conveniently estimated by treating 100 c.c. of the water with a slight excess of $\frac{N}{50}$ hydrochloric acid, boiling the mixture for about one minute, and titrating the excess of acid with $\frac{N}{50}$ barium hydroxide solution. For the estimation of permanent hardness, the water is evaporated with the addition of $\frac{N}{25}$ potassium carbonate solution, the residue then extracted with 90 per cent. alcohol, and the alcoholic solution titrated, after filtration, with $\frac{N}{50}$ hydrochloric acid. The reasons for the adoption of this procedure are that calcium and magnesium carbonates are practically insoluble in 90 per cent. alcohol, that the soluble double magnesium-potassium salt which is liable to form is decomposed by alcohol, with reprecipitation of magnesium carbonate, and that potassium carbonate is more soluble in 90 per cent. alcohol than is sodium carbonate. Total hardness is found from the sum of the temporary hardness and the permanent hardness, or by titrating the precipitate of calcium and magnesium carbonates formed in the estimation of the permanent hardness. An alternative method consists in neutralising the water as in the estimation of temporary hardness, then evaporating it with the addition of potassium carbonate, and estimating the amount of the latter required to precipitate the calcium and magnesium salts. The electrical conductivity of the water, as determined by the Dionic Water Tester (see ANALYST, 1912, **37**, 538), affords evidence as to the degree of hardness of a water. Every 20 units of conductivity correspond, approximately, with 1 degree of hardness.

W. P. S.

Estimation of Calcium and Magnesium in Natural Waters. S. A. Kay and S. H. Newlands. (*J. Soc. Chem. Ind.*, 1916, **35**, 447-449.)—The method depends essentially on the solubility of magnesium carbonate in ammonium carbonate solution, whilst calcium carbonate is insoluble. The total hardness of the water is, first of all, estimated by one of the methods described in the preceding abstract. One hundred c.c. of the water are then evaporated to dryness in a platinum basin, with the addition of 10 c.c. of ammonium carbonate solution (2 grms. of the salt and 1 c.c. of concentrated ammonia per 100 c.c.). The dry residue is treated with 15 c.c. of the ammonium carbonate solution, the mixture heated for two minutes on a water-bath, the solution then decanted through a small filter, and the insoluble portion washed twice with the ammonium carbonate solution. It is next washed with 90 per cent. alcohol until free from alkali, then dissolved in a measured quantity of $\frac{N}{10}$ hydrochloric acid, and the excess of the latter is titrated with $\frac{N}{50}$ barium hydroxide solution, using methyl red as the indicator. The amount of calcium, expressed in degrees of hardness, is then calculated, and the difference between the total hardness and that due to calcium gives the hardness due to magnesium. A simple calculation gives mgrms. of calcium and magnesium per litre of water. W. P. S.

Comparison of the Permanganate Methods for the Estimation of Required Oxygen [in Water Analysis]. J. H. Sachs. (*J. Ind. and Eng. Chem.*, 1916, **8**, 404-406.)—A variety of conditions have been prescribed by various

authors for performing the permanganate test for oxygen absorption in water analysis. The variable factors are: Acidity or alkalinity of the mixture, quantity of permanganate, temperature and duration of the action. Comparative estimations were made with a number of organic substances under these varied conditions. In the alkaline methods there was a tendency to the formation of green potassium manganate, or else an unusually large precipitation of manganese dioxide, which reacts catalytically to reduce further quantities of the permanganate. The alkaline methods were therefore discarded. As regards the temperature, it was found that at 85° and 100° C. much larger quantities of permanganate were reduced than at lower temperatures, especially in acid solution. At 37° C. the quantity consumed was somewhat larger than at the ordinary temperature. Comparative experiments made at 85° C. for one hour and at 37° C. for three hours showed higher results for the higher temperature, but at 85° C. the consumption of oxygen increased largely with the quantity of permanganate present, whereas at 37° C. variation in the quantity of permanganate had but little effect on the consumption value. The author, therefore, expresses a preference for Thresh's method in acid solution at 37° C. The presence of chlorides interferes, but these can be readily removed by treatment with silver oxide. J. F. B.

Estimation of Dissolved Oxygen in Water. J. Miller. (*J. Soc. Chem. Ind.*, 1916, **35**, 457.)—Since phenosafranine, the indicator recommended for use in a method described previously by the author (ANALYST, 1914, **39**, 234), is somewhat difficult to obtain, methylene blue may be used in its place. The two indicators give the same result. W. P. S.

APPARATUS, ETC.

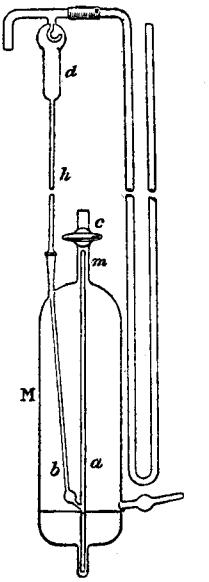
Colour Standards of Colorimetric Assays. H. V. Arny and C. H. Ring. (*J. Ind. and Eng. Chem.*, 1916, **8**, 309-317.)—The authors have already described the solutions employed by them for making colorimetric standards (ANALYST, 1913, **38**, 394, and 1915, **40**, 452), and the present paper deals with the application of such colour solutions to the estimation of ammonia by Nessler's reagent; nitrate determination by the phenol-sulphonic and method; nitrates with sulphanilic acid and a naphthylamine salt; vanillin in conjunction with bromine water and ferrous sulphate; uric acid by Riegler's method, in which phosphomolybdic acid is the reagent employed; salicylic acid together with ferric chloride solution; and finally phosphates when allowed to react with ammonium molybdate. In all cases a comparison of the colour values obtained by the Lovibond tintometer, using red, yellow, and blue glasses, was made beside the authors' coloured solutions. Full details, for which the original paper must be consulted, are given dealing with the variations obtainable under different conditions of dilution, acidity, etc. H. F. E. H.

General Applicability of the Paper Pulp Filter to Quantitative Analysis. S. L. Jodidi and E. H. Kellogg. (*J. Ind. and Eng. Chem.*, 1916, **8**, 317-319.)—Experiments were made in the application of the pulp filter to the quantitative estimation of barium and sulphuric acid as barium sulphate of silver and hydrochloric

acid as silver chloride, and of potassium and ammonium as platinichlorides. The results were found to be as accurate as those obtained with standard filter paper, and, in addition, the pulp filter has the advantage of saving considerable time and labour.

H. F. E. H.

New Safety Valve. M. S. Losanitch. (*Chem. News*, 1916, **113**, 218.)—The device shown in the diagram is adapted to prevent the back-flow of water in water-pumps. The cylindrical vessel M is connected with the pump by means of a rubber tube, and has a glass tap *c* for the admission of air when necessary. It contains a branched tube, not exceeding 2·5 mm. in diameter, one arm of which, *a*, extends almost to the tap *c*, while the other, *b*, is fused through the wall of the vessel and is connected with the tube *h*, so that its total length is about 80 cm. The top of the tube *h* is widened into the space *d*, and is connected with the vessel from which air is to be pumped. Before using the valve, mercury is introduced into the cylindrical vessel until the meniscus is just below the lower edge of the arm *b*. When backflow of water occurs the vessel M is filled, and the pressure forces the column of mercury up the tube, closing both arms, and shutting off the connection with the vessel connected with *d*. With the increase in pressure the mercury rises in the tube *h*, and when it reaches its maximum the tap *c* is opened to allow the water to flow away through the water-pump, and is then closed again, so that communication between the pump and the vessel is again established.



C. A. M.

Unit of Viscosity Measurement. P. C. McIlhiney. (*J. Ind. and Eng. Chem.*, 1916, **8**, 433-435.)—It is often wrongly thought that viscosity measurements, made with the usual practical types of viscosimeters, cannot be simply expressed in terms of the units of absolute viscosity. This, however, is not the case, and it is highly desirable that the indications of the various commercial instruments should be reduced to a uniform standard. The C.G.S. unit of absolute viscosity is inconveniently large, and has no recognised name. A proposal has been made to call it the "poise," in honour of Poiseuille, and this might be adopted. The centipoise (1 cp = 0·01 p) would then be the practical unit, being, in fact, almost identical with the viscosity of water at 20° C. Thus for all practical purposes the viscosity of an oil expressed in centipoises would be its specific viscosity—*i.e.*, its viscosity as compared with water at 20° C. The author has tabulated the equivalents in centipoises of the arbitrary readings given by the Saybolt, Engler, and Redwood viscosimeters, all instruments capable of giving results of sufficient accuracy for industrial purposes. It is suggested that the existence of a universal scale of viscosity would have the result of extending the use of viscosity as a general physical constant outside the field of the oil industry. The tables of equivalents published neglect the effect of

the different specific gravities of the various liquids tested, but the uncorrected viscosities may be corrected, if desired, by multiplying by the density of the liquid at the temperature of the experiment as compared with water at 4° C. J. F. B.

LAW REPORT.

Quality of Milk: The Feeding of Cows. Hunt *v.* Richardson. (*Before* Mr. Justice Darling, Mr. Justice Bray, Mr. Justice Lawrence, Mr. Justice Scrutton, *and* Mr. Justice Avory.) (*Times*, April 17 and June 3, 1916.)—This appeal, by way of case stated from a decision of Justices of the Borough of Cambridge, raised a question of great interest, both to the public generally and to the owners of dairy farms.

Mr. Disturnal, K.C., and Mr. Aggs appeared for the appellant; and Mr. Ricardo appeared for the respondent.

An information was preferred by Ernest Richardson, the respondent, under the Statute 38 and 39 Vic., c. 63, section 6, against John Hunt, the appellant, for that on September 9, 1915, at the Borough of Cambridge, he did unlawfully sell to the prejudice of the purchaser, one David Cox, a certain article of food—to wit, milk—of which a sample was taken by the respondent as an Inspector under the Food and Drugs Acts at the place of delivery in the course of delivery to the purchaser and consigned in pursuance of a contract of sale to such purchaser, which said milk was deficient in milk fat to the extent of 9 per cent., and was not of the nature, substance, and quality demanded. The information was heard on October 13, 1915, and the appellant was convicted and was fined 40s. and costs.

The Facts Proved or Admitted.

At the hearing the following facts were proved or admitted:

1. The appellant was a farmer and cowkeeper living on a farm three miles from Cambridge. He had kept cows there for twenty-five years, and it was his practice to sell all his milk to retail dealers.

2. On September 9, 1915, he had a herd of forty-one good Shorthorn cows, of which twenty-eight were then giving milk. The cows were under the charge of three men, all of whom were competent and experienced in the management and milking of cows. These men milked the cows, and no one else interfered with the milk in any way at any time before the sale to the respondent.

3. The cows were milked twice daily, at 5 a.m. and 1 p.m. The cows were milked into pails, and the milk was poured from the pails into another pail, from which it was strained into churns. When the quantity of milk ordered by each customer had been poured into the churn intended for that customer, all the churns were put into a cart and driven into Cambridge by one of the appellant's men and delivered to the customers.

4. Nothing was added to or abstracted from the milk by the appellant or his servants beyond the abstraction of impurities by the straining. The morning milking was done rather hurriedly. Beyond the mixing required for making up the quantity needed in each churn, there was no general mixing of all the morning milk.

5. In consequence of the heavy rains in the previous July and August, the growth of grass on the appellant's farm on September 9 was "phenomenal in quantity," but it was in a watery condition, and the appellant's cows being fed on it had given a much larger quantity of milk than usual. The cows were given 3 lbs. of cake each per day throughout this season of the year, which was the usual allowance in normal circumstances, and no special steps were taken to counteract the effect on the quality of the milk of the watery state of the herbage or to test by technical means the effect of the watery herbage on the milk.

6. The appellant and his men were well aware of what was taking place, and in spite of this shortly before September 9 the cows were given green maize, which was even more watery, in order to keep up the quantity of milk.

7. The quality of milk is affected by the quantity, and also by the state of health of the animal, the method of milking and the manner of feeding, and the time that elapses between successive milkings. If cows are not thoroughly milked out on any occasion the quality of the milk at that particular milking is poorer.

8. One of the appellant's customers in Cambridge was a retail dealer named Cox. On September 9 the appellant's man drove a churn to Cox's premises and was there met by the respondent, who informed him that he was an inspector, and intended to take a sample of the milk then in course of delivery. The respondent then stirred up the milk in the churn and took a pint of milk, which he divided into three parts, one part of which he had analysed.

9. The analyst certified that the milk was deficient in milk fat to the extent of 9 per cent.

10. The respondent had taken samples of the appellant's milk before and had found them genuine.

11. Milk taken from a healthy herd and mixed should not show less than 3 per cent. of milk fat.

12. Under the Sale of Milk Regulations, 1901, issued by the Board of Agriculture, where a sample of milk contains less than 3 per cent. of milk fat it shall be presumed for the purposes of the Sale of Food and Drugs Act, until the contrary is proved, that the milk is not genuine by reason of the abstraction therefrom of milk fat or the addition thereto of water.

The Contentions.

For the respondent it was contended that new milk deficient in milk fat to the extent of 9 per cent. was an article of food which was not in accordance with the nature, substance, and quality demanded, and although the appellant had supplied it as it came from the cows he had not used proper care in regard to the abnormal conditions prevailing at the time in feeding the cows, but had endeavoured to get quantity without quality, and that, while the milk from a single cow might give less than 3 per cent. of milk fat, it was most improbable that the milk from a herd, if properly mixed, would do so.

For the appellant it was contended that the milk was genuine milk as it came from the cows; that the cows had been properly milked; that morning milk was poorer in quality than afternoon milk; that the condition of this milk, which was morning milk, was due to the abnormal condition of the pastures; that even if the appellant had fed the cows in a particular way so as to obtain a large quantity of milk that was no offence provided that he showed that the milk was supplied as it came from the cow, and that it was not of such poor quality as not to be legal milk at all, and that a mere deficiency of 9 per cent. of milk fat did not warrant the justices in finding that this particular milk was not in fact milk.

The justices were of opinion that the milk was deficient in fat to the amount of 9 per cent., but that the milk was as it had come from the cows without abstraction or addition. They found that the deficiency in milk fat was due to the manner in which the appellant had fed his cows with the object of obtaining a very large supply of milk without regard to quality, and they held, therefore, that the milk was not of the nature, substance, and quality demanded. They therefore held that the offence was proved.

Mr. DISTURNAL submitted that the conviction was wrong. The section did not consider the intent with which an act was done; intention or *mens rea* had nothing to do with it. The regulation of the Board of Agriculture did not lay down that there must always be 3 per cent. of fat; it merely said that if there was less than that percentage the onus of showing that there had been no adulteration was on the vendor. Smithies *v.* Bridge ([1902] 2 K.B., 13; 18 *The Times* LawReports, 575) was not reconcilable with Wolfenden *v.* McCulloch (92 *L.T.*, 857; 21 *The Times* Law Reports, 411), and was wrong. The point had been considered in Scotland in Scott *v.* Jack (49 S.L.R., 989).

THE TEST TO BE APPLIED.

Mr. RICARDO submitted that the conviction was right. This was not genuine milk; and even if it was genuine that was not the test. The test was whether there had been a sale to the prejudice of the purchaser of an article not of the nature, substance, or quality demanded. Quality had been discussed in Anness v. Grivell ([1915] 3 K.B., 685).

Mr. Ricardo then discussed sections 3 to 9 of the Act, and submitted that the vendor could have protected himself by giving notice. The defence that the article was in the condition in which nature produced it was not one of the defences allowed by the provisos to section 6. Knowledge was not an ingredient of the offence. Sandys *v.* Small (3 Q.B.D., 449) dealt with what was to the prejudice of the purchaser. He referred also to Hoyle *v.* Hitchman (4 Q.B.D., 233); Pearks *v.* Ward ([1902] 2 K.B., 1; 18 *The Times* Law Reports, 538); Webb *v.* Knight (2 Q.B.D., 530). Whether an article was of the nature, substance, and quality demanded was a question of fact for the justices. The regulation of the Board of Agriculture merely regulated the procedure on a prosecution; it did not repeal section 6. This milk was not up to the quality which the purchaser was entitled to expect under a contract to supply new milk.

Mr. DISTURNAL replied. The contract of the purchaser was for $5\frac{1}{2}$ gallons of

new milk each morning, and that implied, he admitted, that the milk was to be of commercial quality. But there was nothing to fix the standard except the regulation of the Board, which evidently contemplated that there might be genuine milk with less than 3 per cent.

Judgment was delivered on June 3 in this case.

The Court was now divided, three of their Lordships being in favour of allowing the appeal, while two—Mr. Justice Bray and Mr. Justice Scrutton—thought that the case should be remitted to the justices. By a majority, therefore, the appeal was allowed, and the conviction was quashed.

Each member of the Court had put his judgment into writing. The judgments were of great length, and are recorded in full in *The Times* Law Reports of June 9, 1916, pp. 560-569. Published at *The Times* Office, Printing House Square, London, E.C. Price 9d.

Solicitors.—Messrs. Torr and Co., for Mr. Algernon Lyon, Cambridge; Mr. J. E. Whitehead, Cambridge.

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REVIEWS.

Scientific and Applied Pharmacognosy. By H. Kraemer. Philadelphia: H Kraemer, 1915. Price $5.

No American pharmacognosist is so well known in Great Britain as Professor Henry Kraemer, and no American is so well qualified as he is to give to the world a work on a subject which he has made his own. Professor Kraemer's "Scientific and Applied Pharmacognosy" represents the best in this field of knowledge that America has yet produced, while his "Applied and Economic Botany," published a short time since, may be regarded as a preliminary study of the fundamental principles and facts upon which pharmacognosy is founded.

The book consists of an introduction of eighteen pages, in which the scope, problems, and general principles are set forth, followed by some 836 pages which are devoted to the subject matter. This the author has arranged according to natural orders, a strictly botanical arrangement, but one which his long experience as a teacher has convinced him is the best and most stimulating. The leading characters of each natural order are first described, and these are followed by a more or less detailed description of each drug derived from a plant included in the order. These descriptions constitute naturally the most important part of the work, and demand careful consideration. Taking an important drug such as belladonna leaves as an example, the botanical and geographical sources are first mentioned; then a detailed description of the leaf, flower, and fruit follows; next the inner structure of the leaf and stem is described, after which the powder receives careful attention; then the constituents are dealt with, and here not only are the various alkaloids present enumerated and the proportion in various parts of the plant stated, but the constitution of the alkaloids as revealed by hydrolysis is explained; finally the adulterants (Phytolacca and Scopola leaves) are alluded to. The monograph is accompanied by numerous illustrations of the leaf, the structure, powder, and so on.

The number of drugs dealt with by the author is very large, but it is only the

more important that are discussed so fully; the less important are more briefly but sufficiently described.

Professor Kraemer's work is very comprehensive, and will undoubtedly prove an important contribution to the literature of pharmacognosy. Its value would be still further enhanced by careful editing when the second edition is being prepared. For example, on p. 360 the cyanogenetic glucoside of cherry-laurel leaves is called prulaurasin, which is the term now generally employed, while on the opposite page it is called laurocerasin, no mention being made of prulaurasin; on p. 686 Vitali's test for atropine is given in such a manner that the test would probably fail. Numerous similar instances could be cited, and they constitute a blemish which could, and doubtless will, be removed by careful editing.

H. G. GREENISH.

FOOD ANALYSIS. TYPICAL METHODS AND INTERPRETATION OF RESULTS. By A. G. WOODMAN. First Edition. New York: McGraw-Hill Book Company. 1915. Price 12s. 6d. net.

The preface of this book indicates that it has been written to supply a sound course in the analysis of food-stuffs for the use of students, and intended to explain rather more fully than usual the principal standard methods employed in such work.

A perusal of the book immediately leads to the conclusion that the author has produced a series of analytical studies which, if carefully and conscientiously worked through under the teacher's supervision, would start the young food analyst on his journey with a reliable and sound stock-in-trade of good methods, proper technique, and, further and more important still, of ideas as to how his analytical findings are to be interpreted. In actual fact there are points in the book which might often be welcome to the more advanced traveller on this road.

The methods and style are distinctly American, and frankly a compilation, but the compilation is by one who evidently knows what to take and what to leave, and in not a few places the touch of the actual investigator is clearly seen.

Very full use has been made of Leach's standard work, and in every case references are made to such good text-books of quite cosmopolitan character as will serve to further aid the student when he desires to go deeper into any of his subjects. It is with a sense of gratification that one notices the value that is attached to the Fourth Edition of Allen's "Organic Analysis."

The chapters on General Methods, and especially on the use of the Microscope, are good, and it is pleasant to find the latter instrument introduced to the student at the very beginning.

Whether the selection of only two such fats as olive oil and butterfat would give a student a proper insight into the methods of tackling such difficult problems as arise in oil and fat analysis may be open to question, but at least they serve as an introduction to most of the more important methods used.

The chapter on Milk and Cream may not be quite familiar to English readers, but the methods detailed are sound, and the deductions made from them are quite logically argued, though the student will soon find in practice that Nature is not always as logical as she theoretically is supposed to be.

The same may also be said for the other chapters on Carbohydrate Foods, Cocoa

and Chocolate, Alcoholic Foods, etc. All contain good standard methods, well and thoroughly described, and the inferences to be made are clearly argued.

The book concludes with several pages of very useful (not diagrammatic) photomicrographs of starches, spices, etc.

Errors there are, but they are almost certainly due to oversight in proof-reading, and some of the cross references are misleading, but these do not detract from the general value of the work. It is well printed on good paper, and the illustrations are clear and properly reproduced. Altogether it is much above the usual type of work placed in the hands of students. CECIL REVIS.

INKS: THEIR COMPOSITION AND MANUFACTURE. By C. A. MITCHELL and T. C. HEPWORTH. Second Edition. Pp. xvi + 266. Sixty illustrations, including four plates. London: C. Griffin and Co., Ltd., 1916. Price 7s. 6d. net.

The study of inks is important from many points of view. The student of MSS., the jurist, the chemist, the manufacturer, the printer, are all concerned. In the revised edition of this work Mr. Mitchell has collected much information that must be of great value to each of the above-mentioned.

In a brief but interesting introduction an excellent account is given of the progress of writing and the development of ink manufacture.

The descriptions of the oldest types of inks—that is, those containing carbon as the essential constituent—are particularly interesting, and the interest is enhanced by the excellent illustrations showing Chinese methods of manufacture.

The date when carbonaceous inks gave place, for ordinary use, to the gall inks is not fixed, as the writer states, but it is reasonable to suppose that the discoveries of the alchemists had much to do with the change. Indeed, the recipes given in this book for " home-made " inks are strongly suggestive of alchemy.

In dealing with the modern side of the subject Mr. Mitchell has been at pains to collect a large number of interesting and important results, and amongst these must be included those of his own researches. These latter, moreover, are by no means the least important.

The sections of the work dealing with the tannins and the determination of their amount in inks is very complete. So, too, are those dealing with printing, copying, and marking inks.

Of great interest is the chapter dealing with the examination of writing inks both as fluids and as writing on paper. From the legal point of view the nature of the ink on documents is sometimes of great importance, and to this subject Mr. Mitchell pays considerable attention, without unnecessary detail.

The whole book is most readable, and will well repay study by all who are concerned with the subject. J. P. MILLINGTON.

SAMPLING AND ANALYSING FLUE GASES. By H. KREISINGER and F. K. OVITZ. 1916. (U.S. Bureau of Mines, Bull. 97, pp. 64.)

The introduction to this Bulletin states that it is written for the benefit of those in charge of boiler plants and all other persons interested in detailed information concerning methods of sampling and analysing flue gases and in the utilisation of the analyses in promoting boiler-house economy. With a view to its being understood by persons

who have not had any instruction in chemistry and physics, an endeavour has been made to make it complete in itself by a liberal use of illustrations of apparatus, by the provision of worked examples, and by the explanation of technical terms wherever these are necessarily introduced. So far as any book can accomplish the difficult purpose the authors had in view, this one must be pronounced a success. Were it more bulky, there is little doubt that the majority of the class for which it is written would abandon the attempt to master its contents, even if they had the courage to begin. On the other hand, where everything must be explained from the beginning, it would be difficult to shorten the text without risk of making it more difficult to follow, for the book is singularly free from the redundant matter which mars so many elementary treatises of this type and makes them tiresome to read.

It may, of course, be questioned whether there is any considerable number of persons with no previous chemical and physical knowledge who could attain much success in the sampling and analysis of flue gases, even if provided with so excellent a little book as this. There are some such persons, no doubt, and the type may be more common in America than in Great Britain, but there may be a larger number who would get erroneous results with a risk of seriously misleading those who put confidence in them. This, however, does not detract from the merit of the book. It is only the range of persons to whom it may be of real service that is in question. There must be, especially just now in this country, many persons who have had some practical instruction from a chemist in routine gas-sampling and analysis, and who now find they have to carry on alone without the periodical guidance of the chemist. To such persons the book should be very useful, and they may find in it many explanations that the chemist may not have thought it necessary to give. In a book of this type, misprints are of much more importance than in a book written for chemists, who will recognise nine out of ten misprints as such, and not be misled. The writer has only noticed one misprint, on p. 43, where, under a diagram, for "CO_2 in flue gases, per cent.," "CO, etc.," should be read.

Though written mainly for those with no previous knowledge of the subject, there is matter here of interest to the expert. Thus, experiments are described which support the authors' opinion that whilst the gases from the uptake of a water-tube boiler form a fairly homogeneous mixture (p. 54), those from a fire-tube boiler can rarely be sampled so satisfactorily that the percentage of carbon dioxide found is certainly within 0·5 per cent. of the true average, even when resort is had to elaborate sampling devices, an error of 1 per cent. being only too common (p. 55). They therefore express the view that it is useless to make analyses closer than to the nearest 0·5 per cent. of carbon dioxide, particularly if no determination of the combustible gases is made. The very small improvement effected by elaborate sampling devices for collecting gas from many points in the cross-sections of a flue is worthy of note. The difficulty of keeping such devices clean and in working order is well known, and the authors' experiments suggest that, in some cases at least, they serve no useful purpose.

G. C. JONES.

ERRATUM.—Page 166, last line, 2 per cent. should read 0·2 per cent.