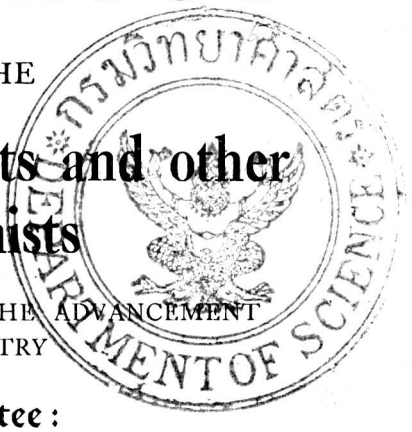
THE ANALYST

THE ORGAN OF THE

Society of Public Analysts and other Analytical Chemists

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT OF ANALYTICAL CHEMISTRY



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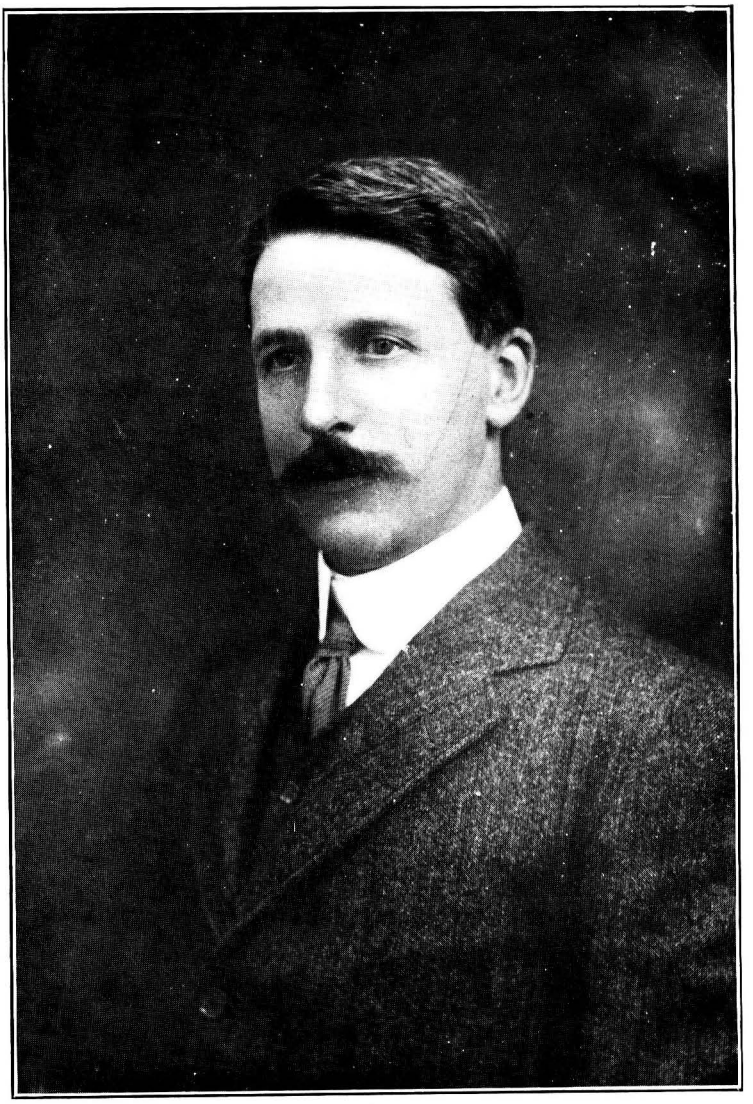


H. Droop Richmond

1867–1931

Hon. Treasurer, 1910–1912
Vice-President, 1909, 1914–1915

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 2nd, the President, Dr. J. T. Dunn, being in the chair.

Certificates were read for the first time in favour of:—Albert Green, M.C., M.Sc., Ph.D., F.I.C., John Farrar Hardwick, B.Sc., A.I.C., Ernest Stephen Hawkins, B.Sc., A.R.C.S., F.I.C., Joseph Robert Johnson, F.I.C., M.Inst.M.M., Arthur Pillans Laurie, M.A., D.Sc., F.R.S.E., and John Morgan Tucker, B.Sc., A.I.C.

Certificates were read for the second time in favour of:—Thomas Whittaker Lovett and William Charles Alfred Wise, B.Sc.

The following were elected Members of the Society:—Charles Hubert Francis Fuller, B.Sc., F.I.C., Ganesh Chandra Moitra, B.Sc., Eric Charles Wood, B.Sc., A.R.C.S., and Robinson Pearson Wood.

The following papers were read and discussed:—"A Micro-method for the Determination of Uronic Anhydride Groups in Pectic Substances," by H. W. Buston, Ph.D., D.I.C.; "The Composition of Linseed Oil," by N. E. Cocchinaras, Ph.D.; "Oil from Malayan *Aleurites Montana* and the Properties of Hong Kong Oil," by T. Hedley Barry; and "The Calcium Fluoride Method for the Determination of Fluoride, with Special Reference to the Analysis of Nickel Plating Solutions," by S. G. Clarke, Ph.D., A.I.C., and W. N. Bradshaw, B.Sc.

NORTH OF ENGLAND SECTION

A MEETING of the Section was held in Leeds on December 5th, 1931. There were 28 present, and the Chairman (Mr. C. J. H. Stock) presided.

Dr. Dunn, President of the Society, read a paper on "The Public Analyst and his Professional Relationships," in which he stated clearly the principles which he suggested a Public Analyst should maintain, drawing illustrations from his own personal experience. Many members took part in the discussion which followed.

A resolution of sympathy was passed with the relatives of the late Mr. W. Foulkes Lowe.

The Identification of Wood and Wood Charcoal Fragments

By J. CECIL MABY, B.Sc., A.R.C.S.

(*Read at the Meeting, October 7th,* 1931)

Introduction.—It is now many years since forest products research, as distinct from the much older science of sylviculture, first began to receive expert attention, and certain common woods to be subjected to anatomical examination;* while, more recently, the physical and chemical properties of wood have been made the subject of special investigations, both in America and in Europe, with an increasing recognition of the enormous value of wood substance, considered either as convertible timber or as a complex of chemical compounds.

The physics and chemistry of wood, however, I shall not discuss in the present paper, my object being briefly to outline the value and importance of a purely anatomical knowledge of the many thousands of commercial woods which have been, and are still, used throughout the world for constructional purposes, cabinet work and the manufacture of innumerable articles of everyday utility.

As is well known to microscopists, each kind of wood possesses its own specific structure and physical properties, the knowledge of which, from originally being a matter of purely botanical significance, was quickly seen to be also of considerable economic and forensic importance.

Thus it was thought possible, by determining the average range of structure and percentage amounts of the various elements in a number of samples belonging to a given commercial species, to deduce therefrom certain *standards* of wood structure for the species, as also in relation to particular purposes and industries. Such standards are still in the process of being worked† out, with an ultimate intention, first, of enabling the selection of the best type and quality of wood for a given purpose; and second, so that sylviculturalists may know more certainly what types of timber are required of them, and how to grow such timber most economically.

Moreover, it has been found that detailed knowledge of the specific structure of commercial woods renders possible the identification of quite minute samples of unknown timber. That such identifications may frequently be of value in commerce, in archaeology, and for forensic purposes, will be easily appreciated. Indeed, in the few years since the inauguration of the two principal institutes in this country,‡ many hundreds of crucial identifications have already been carried out for firms and individuals. For instance, a company may purchase a large consignment of timber purporting to be mahogany, or American white

* *Vide*, for example, the work of Robert Hartig in Germany, upon beech and oak, towards the end of the last century.

† Such investigations are being made in this country upon common ash, elm and oak, in the last of which I have been engaged.

‡ The Forest Products Research Laboratory (D.S.I.R.), Princes Risborough, Bucks., and the Imperial Forestry Institute, Oxford.

oak, say; whereas the consignments may be found by the technologist to be no better than a cheaper and poorer substitute for mahogany (a name often used extremely loosely, since the world's resources of true mahogany have been practically depleted), and, in the second place, American swamp oak—an almost useless timber which, for some undetermined physico-chemical reason, is liable to extreme "collapse"* on seasoning.

Again, pieces of wood and wood charcoal from fallen, burnt and buried edifices, the handles of ancient implements, portions of inhumated and fossilised trees, etc., are constantly requiring identification in order to prove some legal point, to help the antiquarian to solve his historical problems, or to extend our botanical knowledge of the past flora of a country or district.

Not a year passes but many interesting archaeological finds are made in this country alone of charcoals and wood fragments: portions of charred beams and posts, the remains of stockades, piles from lake dwellings, spear hafts, implement handles, charcoals from ancient hearths and furnaces—one and all can be identified. I have, personally, been fortunate in receiving many such remains for examination during the past few years, and can say at once that the instances are few in which interesting information is not thereby acquired. For example, it has been possible to show that red oakwood—presumably *Quercus cerris*—was used in an Elizabethan glass furnace at Hambledon, Surrey, although the tree was not previously supposed to have been introduced until about 1735; while the existence of beech in south-west England long before Roman times has been corroborated by several discoveries, running back to early Neolithic times. In other cases, it has been possible, from the species and apparent sizes of wood employed, to confirm the hypotheses of the excavators as to the nature of the structures in question. Other interesting facts also appear, such as the use of a seemingly Indian wood in a Roman spear-haft found near St. Albans, and the occurrence of now exotic timbers in certain ancient Egyptian structures.

THE PREPARATION OF MATERIAL.—The mode of preparation of material for microscopic examination will depend chiefly upon its physical condition, this being determined by its past history. If it is thought necessary to section a specimen, either for purposes of detailed investigation or for photomicrography and record, the preliminary treatment may then be relatively long and delicate. Often, however—especially with the better-known woods—it is unnecessary for an experienced wood technologist to cut sections at all; a superficial view, obtainable by means of a good hand-lens or low-power binocular microscope, frequently being sufficient to permit of identification. In fact, I have generally found that wood charcoals may best be broken across by hand, to show a clean, clear cross-section of the grain (the most useful view). Practically as much is thus seen superficially as in a thin microscopic section made from embedded material, for the intense blackness of the tissues often renders the more minute structures (*e.g.* pitting of the cell walls) invisible by transmitted light.

* "Collapse" is a remarkable form of distortion and exaggerated shrinkage occurring in certain timbers during seasoning. The phenomenon, which is not to be confused with warping or irregular shrinkage proper, is found to result from an actual collapse of the cell walls—worse in some parts than in others.

An average charcoal sample—even after three or four thousand years under ground—normally preserves every main detail of the wood structure in wonderful perfection, whereas uncharred and sodden wood is frequently found to have suffered considerable internal decay and dissolution, often accompanied by extreme compression and "collapse." Hence, unless the specimens have become partly vitrified or "coaly" (reason unknown) as does sometimes happen, charcoals may usually be said to present better material for identification than excavated wood. Rarely, however, charcoal fragments are dug up in so damp and crumbly a condition that no kind of treatment may avail to preserve their form for microscopic examination. Such specimens are not brittle enough to be broken across, as described above, and they will not always stand slow oven-drying or treatment with alcohol, previous to embedding. The only other alternative seems to be very slow drying in a desiccator, employing hygroscopic salts. But even then the specimens might break up when dropped into the solvent spirit for embedding. This I have not yet attempted.

Very rotten wood samples, as well as charcoals, may also be examined superficially, by breaking across the grain—*never* by cutting, even with the sharpest razor; an alternative method is that of careful impregnation with wax or celloidin, as described below.

In making superficial examinations, whether of wood or charcoal, whereof sufficient detail can thus be observed, a hand lens, though useful, is uncertain and trying to the eyes. A good, low-power binocular microscope, magnifying X 20–30 lin., and having a large field of view (*e.g.* not less than 25 sq. mm.), is, therefore, almost indispensable. The only other, and critical factor, as I need scarcely mention, is the incidence and intensity of illumination.

So far, I have spoken only of superficial examination. Material should, however, be classified as normally requiring one of four kinds of preliminary preparation, according to circumstances. Wood that can be sectioned in a microtome, without preliminary treatment of any kind, must have been wet-rotted in an unusual manner, and is but rarely met with. Even so, the preliminary infiltration of some binding substance is highly desirable.

These four treatments, of which the first two have already been considered, are as follows:—

(1) Brittle specimens of coarse texture or familiar structure.	Break sharply across the grain, in the hand, cleave longitudinally (not cut), and examine superficially.
(2) Tough wood specimens of relatively coarse texture or familiar structure.	Cut transversely with a sharp knife, cleave longitudinally (not cut), and examine superficially.
(3) Normal, tough specimens of wood, whether ancient or modern, of fine texture or unfamiliar structure.	First soften by boiling in water or by treatment with hydrofluoric acid, or both, followed by pickling in glycerin and alcohol. Section on a microtome.
(4) Specimens of fine texture, unfamiliar charcoals, and rotten or crumbling specimens of wood or charcoal.	Embed in either paraffin wax or celloidin, according to relative hardness, and section with a microtome for detailed examination.

With regard to the third group, ordinary wood samples may be said to be either very hard, hard, medium or soft; the first three types are capable of blunting a good steel knife too quickly to enable large thin sections to be cut for microscopic purposes, until the siliceous skeleton, which pervades the entire cellular meshwork, has first been dissolved away by means of hydrofluoric acid. Common oak, for instance, may be classed as "medium to hard," whilst most tropical woods are "very hard." Coniferous timbers, on the other hand, are usually soft enough to cut well after 5 to 10 hours' boiling in water and some storage in a mixture (50:50) of methyl alcohol and glycerin, lasting, say, from a week to twelve months. But the latter solution, being used largely for storage purposes, may, when time is short, be omitted. Moreover, as is well known, glycerin has a softening action upon many organic tissues, and alcohol eventually spoils staining properties; so that storage in this solution can be over-prolonged.

It is usual, therefore, to give the hard woods a treatment of one to four weeks in hydrofluoric acid, diluted down to about 50 per cent. with water, in accordance with the relative hardness of the wood, and to keep the material in hard rubber bottles; this step can be omitted with soft woods. The acid, of course, must be thoroughly washed out before transferring the material to 95 per cent. alcohol, and, finally, to the alcohol-glycerin storage mixture.

Some woods possess sufficient natural colour not to require staining, but wood sections may be suitably stained with iron and haematoxylin, followed by safranine,* and, finally, mounted, after clearing with xylol, in Canada balsam. When less permanent mounts are required, glycerin jelly, mixed with a suitable stain such as methyl blue, may be used as a mounting medium; considerable expense and time are thereby saved.

The degree of softening desirable is ascertained by experience; but, given a really sharp knife and a good sledge microtome (Reichert's models and Jung knives give excellent results), a wood block should cut like rather hard cheese, at a thickness of 10 to 20μ.

It is usual to employ sample blocks of about 10 by 10 by 15 mm. in size, and to cut radial longitudinal, tangential longitudinal, and transverse sections, the last being the most useful for general diagnostic purposes.

Finally, in respect of the fourth class of material: it used, I believe, to be thought that charcoals were too hard and brittle to be sectioned in the usual way, but I found that a solution of commercial cellulose nitrate, known as "Celloidin," made as effective an embedding matrix for charcoals as it does for chitinous insects. The embedding is carried out in the usual way, on these lines: (1) Removal of all air from the tissues with a filter pump, while the samples are in 50 per cent. alcohol. (2) Desiccation, by means of graded alcohols, ending with a mixture of absolute alcohol and methyl ether (50:50). (3) Transference of the samples to air-tight screw-topped bottles, which are kept in an oven at 60° C., and contain celloidin dissolved in ether and alcohol; the concentration of the solution is increased, day by day, from 2 to 16 per cent. (4) Removal of the samples from the 16 per

* A solution of a mixture of the alcohol-soluble and water-soluble safranines, in equal parts, is satisfactory. This, combined with haematoxylin, is excellent for photomicrography. Dilute solutions are best.

cent. celloidin, to be dropped into a mixture of ether and chloroform (50:50), in which they remain until hardened and ready to section.

After sectioning, it is unwise to risk dissolving away the "Celloidin," which may be mounted, infiltrated as it is, with the section, either in glycerin jelly or in balsam. In this connection, I have found that good, clear mounts may be made by using Gurr's mounting medium, which appears slowly to dissolve away the celloidin, so clearing the section.

In microtoming, 95 per cent. alcohol may be used as lubricant, as in cutting ordinary wood blocks; nor have I found the use of the coloured commercial product to affect the results.

A much quicker and cheaper, though less perfect and reliable, technique than the latter is, first, to dry the charcoals, and then to dip them in a dilute solution of celloidin (or of cellulose acetate in acetone), re-painting the cut surface after each section. But, when used in this way, the solution tends to contract on drying, and it does not bind the tissues so thoroughly.

For soft, decayed wood samples, the cheaper and easier paraffin-wax method is suitable. But the technique is too well known for repetition here; xylol is used as paraffin solvent, with warming in an oven, during impregnation, as before.

In addition to these methods, impregnation with a synthetic resin was kindly tried for me, some while ago, at the Building Research Station (D.S.I.R.), where a resin of the following composition (in molecular weight proportions) has been found suitable for the preparation of thin sections of friable and weathered materials:—Phenol, 3; formaldehyde, 6; meta-cresol, 3 parts. In this way the very hardest materials can be successfully embedded and subsequently cut by a steel and diamond wheel, as in petrology; but, as the method is unnecessarily laborious and scarcely so successful as celloidin embedding, it need not be given in detail.

EXAMINATION AND IDENTIFICATION.—The chief diagnostic features, by means of which the wood of one genus may be distinguished from that of another, or—less commonly and surely—that of one species from another, are as follows:—

(i) The relative size, distribution, frequency and configuration of the *conducting vessels* (commonly known as "pores"), as seen in transverse section.

(ii) The relative size, distribution and frequency of the *medullary rays*, as seen in transverse and tangential longitudinal sections.

(iii) The type, grouping and distribution of the *wood fibres*,* as seen in transverse section.

(iv) The amount and arrangement of the vertical *storage parenchyma*, as seen in transverse and radial longitudinal sections.

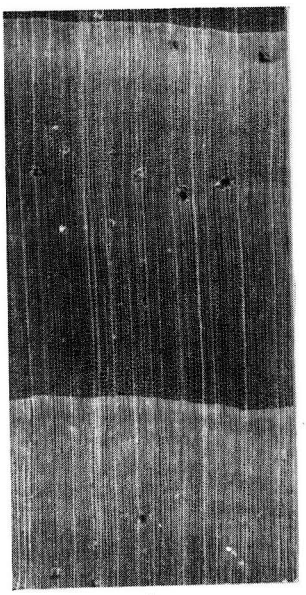
(v) The presence, or absence, and disposition of vertical and horizontal *resin ducts*, as seen in transverse and tangential longitudinal sections.

These features are usually observable with a low-power microscope or hand-lens; but, in very closely similar woods—many of the conifers, for instance—it is

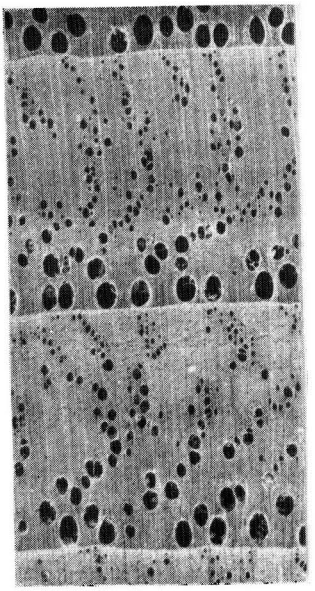
* The fibres are long elements, often occurring in bundles (*e.g.* in oak), which give mechanical strength to the wood. Fibres do not occur in conifers ("soft woods"), being replaced by thick-walled tracheids.

PLATE I.

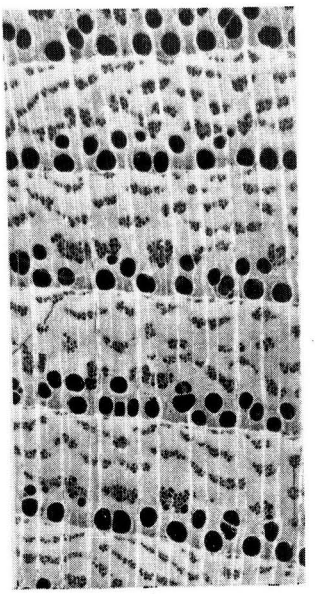
STRUCTURE OF WOODS



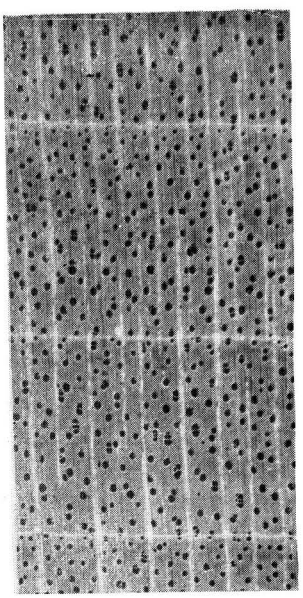
1
Scotch pine
(*Pinus sylvestris*)



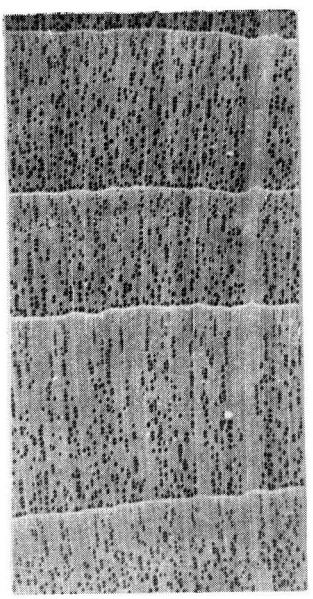
2
Sweet chestnut
(*Castanea vesca*)



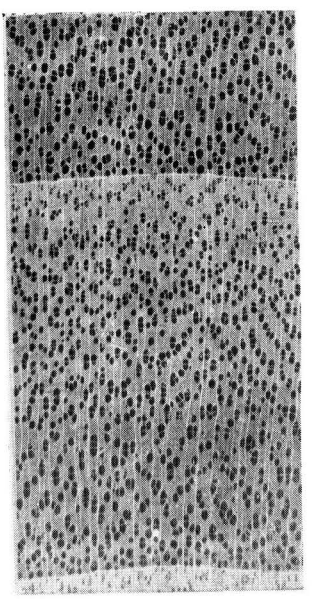
3
Common elm
(*Ulmus campestris*)



4
Field maple
(*Acer campestre*)



5
Hazel
(*Corylus avellana*)



6
Black poplar
(*Populus nigra*)

All are transverse sections, × 10 linear, as viewed under surface illumination.

often necessary to make use of yet more minute structures, such as are only visible in a good section and at high magnification; as, for example, pits in the cell walls, the height, width and frequency of the small rays, and the form of the cells composing the latter.

But, in not a few instances, two distinct species may resemble one another so closely that even these minute distinctions fail. Thus, from knowledge of the wood structure of a single small sample, it is often unsafe to deduce more than the broad *genus*. For instance, many species of elm are hard to differentiate, so are certain oaks; whilst the poplars and willows not only cannot safely be distinguished specifically, but poplar and willow woods may also be generically indistinguishable in surface view. And so on with other groups of closely related genera. The two related species, evergreen oak (*Q. ilex*) and white oak (*Q. alba*), however, would not readily be confused.

Reference to Plate I will illustrate the following diagnostic features:— Coniferous woods ("softwoods") are immediately distinguishable as a group from the Angiospermous flowering trees ("hardwoods") by the fact that they never possess vessels ("pores"), though they may, or may not, contain resin ducts— a group and generic distinction. (See Fig. 1.) Again, in a conifer, the more recently-formed wood of a growth-ring may, or may not, be sharply contrasted with the rest of the ring in the colour or thickness of its cell walls, or both. In conifers, the rays are always fine (Fig. 1); in the Angiosperms, they are sometimes fine and numerous (Figs. 2 and 6), sometimes thicker and less numerous (Figs. 3 and 4); and, occasionally, very large rays, visible to the naked eye, alternate with small ones (Fig. 5).

It will also be seen, from Plate I, that the "pores" in hardwoods are of variable size and arrangement, ranging from "diffuse porosity" (Fig. 4), by way of transitional forms (Figs. 6, 5 and 2), to marked "ring porosity" (Fig. 3)—*viz.*, a sharp transition, at the beginning of the ring, from large to small pores.

More detailed features need not be enumerated here. But one should add that, owing to the enormous number of woods of economic utility, it is a great help to the wood technologist in identifying unknown samples to be told, if possible, the country of origin. Yet, even that is of little avail when the region happens to be India, S. America, or Africa, for example, where the number of indigenous species runs into thousands, and whence others are still being imported. In all such cases, therefore, it is usual to construct both macroscopic and microscopic "keys," based upon the various anatomical characteristics mentioned above, *plus* features such as colour, hardness, taste, smell and density. These "keys," when comprehensively planned, facilitate the rapid identification of unknown wood samples. But individual variation and aberration from type are serious obstacles; a large collection of authentic wood samples and microscopic sections is, therefore, desirable in order that the wood technologist may also check his conclusions.

NOTES ON THE ILLUSTRATIONS.—*Plate I* represents surface views of small fragments of six common European woods, as seen in transverse section, magnified × 10 linear.

Plate II shows still smaller areas from transverse sections of three English woods (two being slow grown, with very narrow rings), as seen under the microscope by transmitted light, magnified × 30 lin. But, in this plate, only the upper three figures depict normal wood; the lower three are Roman charcoals of the same woods, submitted to me for identification, in which, similar, only slightly shrunken, tissues and elements may be recognised.

The charcoals were derived from a Roman smelting furnace, dating back to about 300 A.D., discovered in Surrey, and I am indebted to Mr. S. E. Winbolt for permission to use these photomicrographs, as well as to the Director of the Forest Products Research Laboratory, England, and Prof. C. C. Forsaith, of New York State College of Forestry, under whose direction the work here described was initiated.

3, RAWLINSON ROAD,
OXFORD.

DISCUSSION

Dr. CAMERON asked if there were any method for identifying charcoal when finely powdered.

Mr. MABY replied that this was very difficult, although occasionally in the case of an easily identifiable wood, such as common oak, he had been able to identify small splinters.

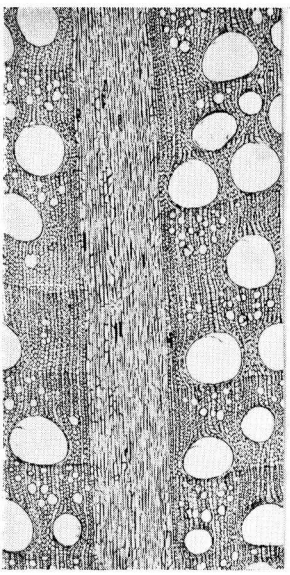
ADDENDUM.—Since the meeting my attention has been directed to a paper on "The Identification of Norit and other Wood Charcoals," by H. G. Tanner (*Ind. Eng. Chem.*, 1925, **17**, 191; ANALYST, 1926, **51**, 50). In an attempt to determine the nature of a highly activated decolorising charcoal called "Norit," which was introduced about 1911, it was found that minute particles of cell wall substance (apparently from the walls of conducting vessels or tracheids), termed "identification particles," were always present. These particles, examined under a high power of the microscope (say, ×500), were seen to be perforated by numerous minute pits, the relative size, frequency and pattern of which were seen to constitute a generic, if not also a specific, character. In this way it was concluded that "Norit" had been made from birch wood (*Betula occidentalis ?*).

I should add that I have not yet had occasion to employ the method myself, and a considerable amount of systematic work would be required before it could be put into practice; but, judging by what I have seen of cell-walled pitting in woods, it should prove satisfactory.

One possible objection which occurs to me is that the size, form and arrangement of such pits undoubtedly vary to a considerable extent within a given species, or even from part to part of a single cell wall. Moreover, a considerable amount of shrinkage (about 1/3?) takes place in wood when it is converted into charcoal. In incompletely charred specimens, therefore, the mean diameter of such pits might be greater than in specimens which have been treated for a longer period of time.

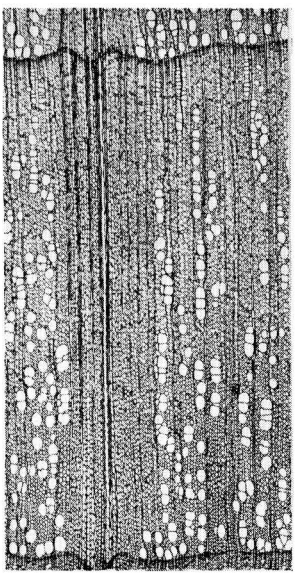
STRUCTURE OF WOODS

A



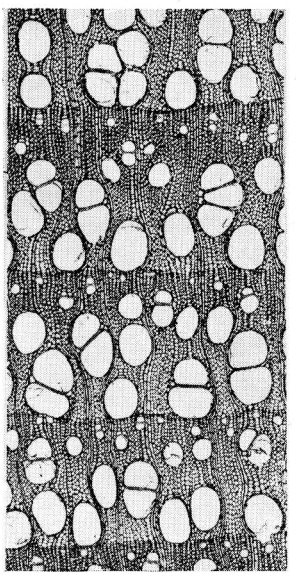
Common oak
(*Quercus* sp.)

B



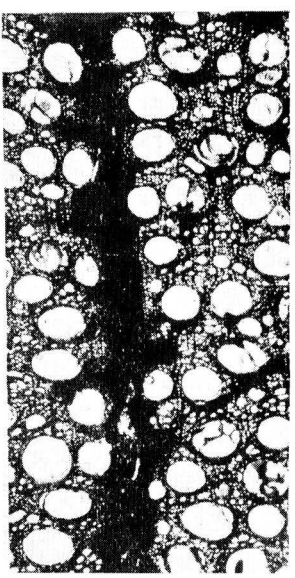
Hazel
(*Corylus* sp.)

C

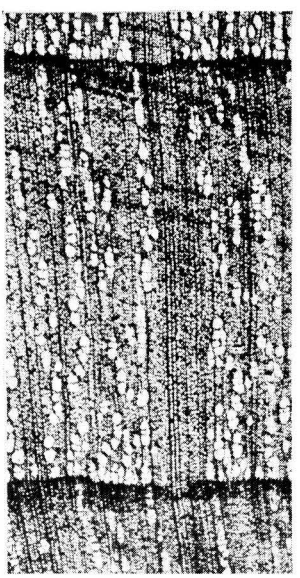


Ash
(*Fraxinus* sp.)

a



b



c

Below: Roman charcoals (*a*, *b*, *c*) for comparison with the woods (A, B, C) shown above.

All are transverse sections ×30 linear, as viewed by transmitted light.

The Extraction and Determination of Vanillin in Chocolate and Cocoa Butter

By D. M. FREELAND, F.I.C.

(*Read at the Meeting, November 4th,* 1931)

The flavour of vanilla is one that persists in popularity, especially in Britain. It is conveyed to chocolate and confectionery as vanillin, macerated vanilla pods, or as essences and extracts from the pods, which may be fortified with vanillin. Other natural materials containing vanillin, such as benzoin, may also be employed. The quantity of vanillin added seldom exceeds 0·1 per cent. of the finished article, as an excessive quantity results in an unpleasant after-flavour and affects the throat in an irritating manner.

Vanillin, resulting from the flavouring agent added to chocolate, is dissolved by the cocoa butter, and any method devised for its extraction must be able to cope with impurities inherent in a fatty solvent, especially those which lead to the production of emulsions. For the purpose of establishing a method of extraction, a 1 per cent. solution of vanillin in filtered, molten cocoa butter was prepared.

Vanillin is soluble in water to some extent. Durrans (*Perf. & Ess. Oil Rec.*, **1924, 15,** 239) quotes as its solubility 1·5 per cent. at 20° C., and 3·3 per cent. at 40° C. Shaking out the flavoured fat with warm water resulted in the recovery of a mere trace of vanillin. Winton and Silvermann (*J. Amer. Chem. Soc.*, 1902, **24,** 1128) have recommended the use of a 2 per cent. aqueous solution of ammonia for the removal of vanillin from de-alcoholised vanilla extracts.

Sufficient petroleum spirit (b.pt. 40°–60° C.) was added to 10 grms. of the flavoured cocoa butter to prevent solidification, and, after transference to a separating funnel, it was extracted with 2 per cent. aqueous ammonia. Emulsions formed, being assisted by the free fatty acids in the cocoa butter. These were difficult to disperse, but the addition of a little amyl alcohol materially assisted the separation.

Ammonia solutions of 2 per cent. (NH_3) concentration were prepared by adding the requisite quantity of ammonia solution (sp. gr. 0·880) to (*a*) methyl alcohol; (*b*) 50 per cent. (by vol.) aqueous alcohol; (*c*) 95 per cent. (by vol.) alcohol; and separate quantities of the flavoured fat were extracted by these solutions, respectively. The 95 per cent. alcohol and ammonia showed a sharp separation from the cocoa fat solution, and the tendency to form emulsions was small.

The following are details of the method finally adopted for the extraction: Twenty-five grms. of the melted fat are transferred to a cylindrical separating funnel of about 100 ml. capacity by means of petroleum spirit (b.pt. 40°–60° C.), using sufficient to prevent solidification of the fat when cool and to reduce its viscosity. An alcoholic ammonia solution containing about 2 per cent. of ammonia

is prepared by diluting sufficient ammonia solution of 0·880 sp. gr. with 95 per cent. (by vol.) alcohol. The fat solution is shaken out with successive quantities of 10, 5, 5 and 5 ml. of the alcoholic ammonia, care being taken that as little fat as possible is removed when running off the alcoholic extracts into a glass evaporating basin of about 120 ml. capacity, in which they are united. If it is seen that globules of the alcohol remain dispersed to an extensive degree in the bulk of fat solution, the viscosity of that solution may be reduced by small additions of petroleum spirit, and this, combined with gentle agitation, will cause the globules to deposit. Forty ml. of water containing 18 ml. of *N* hydrochloric acid are added to the contents of the basin. Alcohol is then removed by evaporation upon a water-bath at 70° C. until the contents in the basin have been reduced to 20 ml. The liquid in the dish, with which are associated some oily globules (which experiment has shown cannot be neglected without loss of vanillin) is transferred to a separating funnel by means of warm water, followed by two or three washings with ether. When cool, more ether is added to the separator, which is then stoppered and shaken. The ethereal layer is separated, and three ethereal extracts of the aqueous portion are obtained. To the ethereal extracts, united in another separating funnel, are added 10 ml. of water, followed by 2 to 3 ml. of 2 per cent. aqueous ammonia (2 per cent. NH_3). After shaking out, the separated aqueous layer, together with any emulsion which accompanies it, is run into another separator, and the ether is extracted three times more, 5 ml. of water and 1 ml. of the dilute ammonia being used for each extraction. To the united and somewhat emulsified ammonia extracts is added saturated brine in sufficient quantity to "salt out" the emulsion. The almost clear aqueous layer is drawn off into a separating funnel, and followed by two small brine washings of the emulsion. The ammonia-brine extract is rendered just acid to methyl orange by addition of hydrochloric acid, and is extracted four times with ether, quantities of 15, 15, 10, 10 ml., respectively, being used. These ethereal extracts are put into a dry, tapped funnel, from which aqueous drainings are run off carefully. The ether is decanted into a weighed glass evaporating basin, followed by ethereal washings from the tapped funnel. The ether is allowed to evaporate spontaneously from the dish, floating on warm water, until about 3 ml. remain therein, and this is dissipated in a vacuum desiccator over sulphuric acid. When dry, the dish is allowed to gain equilibrium in the balance case, and the weight of crude vanillin is obtained.

The following results were obtained by the extraction of the prepared cocoa butter which was diluted with unflavoured butter, as detailed:

Flavoured cocoa butter. Grms.	Unflavoured cocoa butter. Grms.	Total fat extracted. Grms.	Vanillin content. Grm.	Crude vanillin recovered. Grm.
10	—	10	0·1	0·126
10	15	25	0·1	0·0998
5	20	25	0·05	0·0562
5	20	25	0·05	0·0596
5	20	25	0·05	0·0525
5	20	25	0·05	0·0493
5	20	25	0·05	0·0530

DETERMINATION OF PURITY.—The variation in the weights of crude vanillin from these different extractions proved that a method of determining the actual vanillin present was required. The risk of fatty acids being present with the vanillin in the crude extract prevented the use of a simple titration of the hydroxyl group, as suggested by Wellmann (*Pharm. Zeit.*, 1898, 634). Determination of the methoxy group by operations based on Zeisel's classic process called for special apparatus, as a micro-method was indicated. S. B. Phillips (ANALYST, **1923, 48**, 368) reviewed methods depending on the aldehyde group, and described novel volumetric and gravimetric procedures, involving combination with that group. Many colorimetric methods have been recorded, but experience with some of these, when applied to vanilla essences, has revealed inherent failings in them.

H. J. Wichmann (*J. Assoc. Off. Agric. Chem.*, 1921, **4**, 479) has suggested that sublimation affords a suitable means for the purification of vanillin. Quantities of 0·05 grm. of vanillin (prepared from eugenol) were subjected to sublimation in the apparatus devised by Monier-Williams for the purification of benzoic acid (ANALYST **1927, 52**, 229). Conditions of temperature and duration of heating were varied, but not more than 0·034 grm. was recovered by this means. It was evident that part of the vanillin decomposes into guaiacol under sublimation conditions.

Attention was next focussed on Phillips's methods (*loc. cit.*), and attempts were made to adjust them to the small quantities of vanillin present in the crude extract. For the gravimetric process, Phillips takes 1 grm. of vanillin in a small beaker, adds 13·6 ml. of 0·5 *N* sodium hydroxide solution, and warms to assist solution. A solution of 2·4 grms. of semicarbazide hydrochloride and 5 grms. of crystalline sodium acetate in 30 ml. of water is filtered and stirred into the vanillin solution, and the mixture is heated in boiling water for ten minutes. After cooling, complete precipitation takes 4 hours, and the resulting precipitate is filtered off, washed free from chloride, and dried for 2 to 3 hours in a water-oven until constant in weight. The amount of semicarbazone, multiplied by 0·7271, gives the vanillin.

A tenth of the quantities of reagents given above were used when applying this procedure to crude vanillin residues obtained from 10 grm. quantities of flavoured cocoa butter. Upon adding the semicarbazide reagent to the warm vanillin solution, some precipitation was at once evident. The precipitate was inclined to be tacky, and in the first experiment was collected and filtered off with the semicarbazone, which separated upon cooling. In the second experiment only the flocculent and easily filterable semi-carbazone was collected. This procedure is open to criticism, and the adoption of the method was not further pursued, as the volumetric method, then in course of trial, was showing promise of giving speedier and better results. Typical results of the gravimetric experiments are indicated below:

Exp.	Extracting medium.	Crude vanillin recovered. Grm.	Vanillin from semi-carbazone. Grm.	Actual vanillin. Grm.	Recovery. Per Cent.
1.	Aqueous ammonia	0·180	0·1216	0·1	121·6
2.	Alcoholic ,,	0·126	0·0960	0·1	96·0

VOLUMETRIC METHOD.—One grm. of vanillin is dissolved in 20 ml. of 80 per cent. (sp. gr. 0·8484) neutral and pure alcohol. Inherent organic acidity is removed by the cautious addition of 0·1 *N* sodium hydroxide solution, with methyl red as indicator, and 1·1 to 1·2 grm. of pure *p*-toluidine is dissolved in the liquid. Twenty ml. of 0·5 *N* sodium hydroxide solution are added, and 100 ml. of cold water (free from carbon dioxide) are poured in. The liquid is then titrated rapidly (to avoid absorption of carbon dioxide) with 0·5 *N* sulphuric acid until a permanent turbidity is noted. The difference between the volumes of 0·5 *N* alkali and acid, multiplied by 0·076, gives the amount of vanillin present.

Upon trying this method, using small quantities of vanillin, the conditions outlined above had to be altered materially in order to obtain the turbid end-point. The influence of the quantity of alcohol present was most marked, and, if in slight excess, the production of the end-point was entirely nullified, although the depth of tint indicative of it was maintained; the addition of excess of water, or a similar effect obtained by the use of too great a volume of standard alkali, also destroyed the end-point turbidity.

The conditions adopted for a satisfactory end-point, as applied to weighed quantities of vanillin, are as follows:—The vanillin, weighed upon a watch-glass, is transferred to a clear glass specimen tube, 4″ × $\frac{7}{8}$″, by means of the necessary quantity of 80 per cent. alcohol, as shown below. A drop of methyl red indicator is added, followed by sufficient 0·02 *N* sodium hydroxide solution to effect the neutral colour change. Then, pure *p*-toluidine, weighed within 0·01 grm. in excess of the vanillin taken, is added to the tube, dissolved by shaking, and 5 ml. of 0·1 *N* sodium hydroxide solution are added from a burette, followed by the amount of water indicated below. The liquid is back-titrated to the turbid end-point with 0·05 *N* sulphuric acid, added from a burette graduated in 1/20th ml. (1 ml. of 0·05 *N* alkali = 0·0076 grm. of vanillin).

Vanillin. Grm.	Alcohol (80 per cent.). Ml.	Water. Ml.
0·04	0·8	–
0·05	1·0	1
0·06	1·2	2
0·07	1·4	2

The following results were obtained:

Vanillin taken. Grm.	0·1 *N* NaOH taken Ml.	Back-titration 0·05 *N* H_2SO_4 Ml.	Combined 0·05 *N* NaOH, from mean back-titration. Ml.	Vanillin found. Grm.
0·04	5	4·65 4·63	5·36	0·0407
0·05	5	3·36 3·46	6·59	0·0501
0·06	5	2·06 2·07	7·93	0·0603
0·07	5	0·71 0·68	9·30	0·0707

Certain slight modifications are necessary when applying the method to the determination of the vanillin present in the crude extract. If the residue is taken up in 80 per cent. alcohol, impurities dissolve with the vanillin and produce a turbidity in the solution before the final titration can be applied. Impurities are eliminated in the following manner:

The crude residue in the glass basin is extracted with 2 ml. of alcohol (40 per cent. by vol.). It is advisable to warm the basin slightly; the residue is thus loosened from the side, and part appears as oily globules on the surface of the alcohol. After cooling to about 15° C., the liquid is decanted through a disc of filter paper in a small Hirsch funnel, which, with an accompanying tube for attachment to a water-pump, passes through a double-bored stopper fitting the specimen tube. The residue in the basin is extracted thrice more in like manner, using 1 ml. of 40 per cent. alcohol each time, and pumping each washing dry from the funnel before adding its successor. Alcohol is then evaporated from the contents of the tube. This is done expeditiously by aspirating air through the tube, which is placed in a water-bath at about 50° C., until a volume of about 2 ml. remains. Free acidity is neutralised, and a suitable quantity of *p*-toluidine is added. This quantity approximates the weight of the crude extract, and if this is under 0·04 grm., the *p*-toluidine should not exceed its weight. Strong alcohol is added, drop by drop, until, on shaking, solution takes place. At this point the anhydro complex may be thrown out as a canary-yellow precipitate. From this point the procedure for final titration, as detailed above, is followed.

Typical results obtained are tabulated below:

Actual vanillin in cocoa butter. Grm.	Crude vanillin extracted. Grm.	Vanillin found by titration. Grm.	Recovery. Per Cent.
0·05	0·0793	0·0421	84·2
0·05	0·0530	0·0426	85·2
0·05	0·0562	0·0436	87·2
0·05	0·0596	0·0479	95·8
0·05	0·0525	0·0456	91·2
0·05	0·0493	0·0424	84·8
		Mean	88·0

With regard to the first result above (showing 84·2 per cent. recovery), the vanillin was first extracted from the crude material by sodium bisulphite. The bisulphite compound was decomposed, and the vanillin recovered weighed 0·042 grm. This, when dissolved and titrated, gave 0·0421 grm. of vanillin.

It may be concluded, therefore, that the extraction process previously described results in the recovery of 88 per cent. of the 0·2 per cent. of vanillin contained in cocoa butter.

VANILLIN FROM CHOCOLATE.—The fat from chocolate is first extracted. Most of it can be removed simply by placing the broken-up chocolate in a flask, covering it with petroleum spirit (b.pt. 40° to 60° C.), warming gently, and shaking the contents until the solid lumps have disintegrated. The chocolate suspension is transferred to a tall glass cylinder, and the solids are left to settle overnight. By applying slight suction to a flask, the clear fat solution can be drawn over by means

of a tube, bent up at the end, and inserted carefully to such a depth in the cylinder that the solids remain undisturbed. Further shakings with solvent, settling and withdrawal of the supernatant liquid can be given, if desired, until the chocolate is exhausted. The fat solution is filtered, and the solvent is recovered at a low temperature. The last traces of solvent are removed from the fat by applying heat which is insufficient to cause loss of vanillin by volatilisation.

The amounts of vanillin in the cocoa butter thus obtained from two chocolates were determined.

Chocolate A.—Cocoa butter content = 31·09 per cent.

Extraction No.	Cocoa butter extracted. Grms.	Crude vanillin obtained. Grm.	Vanillin content of crude extract by titration (in 25 grms. butter). Grm.
1.	25	0·0420	0·0289
2.	25	0·0410	0·0306
3.	25	0·0660	0·0303
		Mean	0·0299

Vanillin content of chocolate according to mean recovery = 0·0372 per cent.

Chocolate B.—Cocoa butter content = 32·33 per cent.

1.	30	0·0085	0·0068
2.	25	0·0072	0·0055
3.	25	0·0060	0·0049
4.	25	0·0216	0·0057
		Mean	0·0057

Vanillin content of chocolate according to mean recovery = 0·0075 per cent.

The high crude vanillin weights obtained in extractions A3 and B4 are explained by the use of stronger aqueous ammonia, which resulted in more impurity being carried forward in the subsequent extraction stages. The low weight of crude vanillin obtained by the extraction of the cocoa butter from Chocolate B necessitated adjustment of the quantities of reagents used for the titration process. Thus, 1 ml. of 0·1 *N* sodium hydroxide solution was employed, instead of 5 ml., as indicated in the procedure.

The results obtained from the chocolates can be adjusted by taking into account the figure of 88 per cent., the mean recovery of vanillin from cocoa butter containing 0·2 per cent.

The method described for the extraction should serve equally well for fatty materials other than cocoa butter which contain dissolved vanillin.

I wish to thank the Directors of Messrs. Macfarlane, Lang & Co., Ltd., for permission to publish these results.

THE LABORATORY,
MESSRS. MACFARLANE, LANG & CO., LTD.,
FULHAM, S.W.6.

Discussion

Mr. C. E. Sage asked if there were any means of detecting vanillin made from the vanilla bean, as apart from the three synthetic kinds of vanillin. He, personally, had to rely on his sense of smell to distinguish between the four kinds of vanillin in use, but he would like to know if this could be done chemically.

Mr. G. N. Grinling asked whether the method would be of any use for the cream fillings used in biscuits, Swiss rolls, etc. Also, had it been applied to vegetable oils, as apart from cocoa butter, or to substances on the market claimed to be four times as strong as vanillin? Had the author considered centrifuging as a means of accelerating the separation? He had frequently centrifuged fats in cocoas, and got good results very much more quickly than in the manner described.

Mr. Freeland, replying to Mr. Sage, said that he was unaware of any chemical means of distinguishing vanillin derived from the vanilla bean from that manufactured synthetically. He suggested, however, that little vanillin was extracted from the vanilla bean for use as such, as anyone desiring to use the natural principle would surely employ the bean.

Replying to other questions, he said that, provided moisture was eliminated from cream fillings, it was possible to follow the process indicated for cocoa butter. Many of the vanillin substitutes on the market consisted of ethyl-vanillin. He had not tried his method on this substance. He acknowledged that centrifuging would be helpful, but he had not been able to do this on account of the volume of liquid being too great.

Food Control in Holland

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(*Abridged from the Paper read at the Meeting, February 4th,* 1931)

Prior to the Dutch Pure Food Act of September 19th, 1919, the legal basis for the fight against the adulteration of food rested on municipal decrees in several towns, and lacked sufficient juridical support.

The principal paragraphs of the new Act forbid and impose severe penalties for the sale of foodstuffs which may be injurious to health, or are of incorrect composition or are unsound. Foodstuffs are considered to be of incorrect composition, not only when they are adulterated, but also when they are naturally defective, as, for example, if the proportions of their effective constituents are below the accepted standard for the trade. The definition given in that Act, of the term "incorrect composition," was made very elastic, so that the Directors of the Food Inspection Services might use different standards so long as no Order in Council had established legal standards for all the various articles, as by now has practically been done. The initial difficulties have been surmounted by agreements between the directors of Food Services and reputable large manufacturers, and some of these local trade standards have subsequently served as the basis for Orders in Council.

It should be mentioned that the Dutch Act, although described as the Pure Food Act, was in reality projected with a wider scope. Any article of commerce can, by Order in Council, be brought within the range of this law, and then has to comply with the conditions laid down in the principal paragraph of the Act, *viz.* that it must be of correct composition and in sound condition, and not liable to cause injury to health when used for its normal purpose. Up to the present the following articles, other than foods, have been brought, by Orders in Council, within the scope of the Act:—(1) All articles intended to be used or used in the preparation of food or drink; (2) all articles intended to be used or used for the packing of food or drink; (3) wallpaper and curtains; (4) toys; (5) rubber articles used in connection with the feeding of infants; (6) toilet articles and cosmetics; (7) spoons, forks and other household implements; (8) articles for washing and bleaching, and for polishing and dyeing of leather; (9) substances for destroying insects and other noxious animals; (10) kapok.

For some of the articles in this list special limits and standards have been fixed, such as, for example, for the arsenic content of wallpapers and tapestries, and for the composition of soap, washing and bleaching powders, and kapok. In addition, there is an Order in Council, the so-called General Decree, on the hygienic conditions of shops where food is sold, and very severe regulations have been made for the milk trade, so as to ensure progressive improvement in the hygienic production, transport and distribution of milk.

The Act makes it obligatory on municipalities to organise the inspection of foods, and authorises penalties not exceeding a fine of 2,000 fl. or 6 months' imprisonment. All municipalities have the same regulations controlling the sale and distribution of food, etc., or of articles which, although used for their proper purpose, might be injurious to life or health. The basis of the control is thus both national and municipal; it ensures national unity in standards, but leaves to the local authorities the power of accommodation to local conditions.

The Control is carried out by twenty-one Food Inspection Services, each of which controls the trade in its central municipality by means of a technical inspection staff and a chemical staff. Before any prosecution is instituted independent analyses are made by two chemists. The vendor is entitled to require the inspector to seal a second sample to be left with him. Inspectors have the power of entering at any time premises where food is prepared or kept, but, if the occupier of the premises also lives there, the inspectors can enter only after producing a written permit signed by a judge or mayor.

The Orders in Council are based on drafts drawn up by a Commission which acts in co-operation with representative manufacturers and tradesmen, and these drafts are first submitted to the trade organisations.

The Act authorises a manufacturer or a group of manufacturers to prepare their products under the supervision of a private institute, and to publish an announcement to this effect. So far, no one has taken advantage of this permission.

The appointment of the Director of a Food Service has to be confirmed by the Government. The inspection services, however, are administered by the respective central municipalities. The Government pays half of the yearly expense, and the

other half is paid by the municipalities belonging to the district of the inspection department, according to the number of their inhabitants.

The smallest service is that in Leyden, with a population of 208,000; the largest that in Amsterdam, with a population of 835,000. In 1929 the Food Inspection Department in Amsterdam inspected 548,090 lots of foodstuffs, and 41,849 samples, of which 28,204 were milks, were examined in the laboratory.

INSPECTION OF MILK.—Although the inspectors have power to make a preliminary examination of all articles, in practice this is done only with milk. The inspectors test milks with the lactometer, and also apply Storch's reagent (in the form of powder) to ascertain whether the milk or cream is pasteurised (73° C.), but there is a rule that the inspectors have to bring in samples not only of suspected milk, but also of milk that seems to them from the lactometer reading to be genuine. Among these unsuspected samples there may be some which have been brought to the correct specific gravity by the addition of both water and skim milk. As a matter of fact, several skilful adulterators have confessed that they worked in this way for many years without ever coming into conflict with the Inspection Department. Most of them were found out by the cryoscopic method, which is in daily use in every laboratory for milk analysis in Holland. It is not necessary, of course, to "freeze" every one of the hundred, or so, samples brought in each day, but it seems reasonable to suspect of being watered every milk which gives a result for solids-not-fat 0·20 below the mean result for genuine milk samples of the same day. Indeed, by statistical examination of the results given by milk from farmers it would be possible to prove that milk diverging by more than 0·2 per cent. in solids-not-fat, or by 0·3 per cent. in fat, may be suspected of adulteration. If all the analyses of farmers' milk over a period of a few days are plotted as a graph, an ellipse can be drawn in such a way that half of the samples are inside, and the other half evenly distributed in different directions outside the ellipse. It is reasonable to regard the latter as abnormal, and, in so far as their analytical results are low, as suspicious or incorrect. We have drawn such ellipses for each of the months of different years, and have found that, although, of course, their centre changes with the mean composition of the milk in different seasons, their dimensions are fairly constant, so that the critical number of 0·2 for solids-not-fat and 0·3 for fat may be used throughout the year for Dutch farmers' milk, sampled from the original 50-litre cans.

When the Food Inspection Service in Amsterdam, in its present form, first came into operation (in 1921) the statistics showed that about 40 per cent. of the milk samples taken were adulterated. From that time onwards 30,000 samples a year were analysed in the laboratory, with the result that in 1930 only 3 per cent. of the samples were condemned as adulterated.

In 1924 the hygienic examination of milk was begun. The milk is first examined for visible dirt, and the numbers of streptococci and bacteria are determined (standard: less than 1,000,000 bacteria per c.c., or, what comes to about the same thing, a reductase time of less than 3½ hours, as determined by a slightly modified form of Barthel's method).

More recently some 300 samples per annum have also been tested for tuberculosis bacilli, and the number is to be increased in future. Improvement has already

resulted from these examinations. The percentage of samples containing streptococci decreased from 13 per cent. in 1926 to 7·5 per cent. in 1929. About 70 per cent. of the samples of raw milk were bacteriologically sound (low reductase number). For the last four years stalls and utensils have been systematically controlled by a special stall inspector, and it is now estimated that 70 per cent. of the stalls and of the cattle reasonably satisfy the requirements. Further improvement is somewhat handicapped by the difficult economic position of dairy farmers.

Milk from farms within 20 miles of Amsterdam is best delivered raw in the original cans sealed with a lead seal bearing the farmer's initial. Milk coming from other districts must be pasteurised, unless a special permit has been obtained for it to be imported in the raw condition. Pasteurised milk (Storch test,* negative, 25,000 bacteria per c.c.) and pasteurising plants are also supervised. About 16 per cent. of the milk is supplied in the pasteurised state.

General Inspection Work.—The inspectors visit each grocery shop at least once a quarter, and dairies and bakeries once or twice a month. A prosecution is only instituted when it is clear that a simple warning is ineffective. By means of such written and verbal warning *bona-fide* traders have gradually been taught how to comply with the rules for composition and labelling promulgated from time to time for special categories of foodstuffs.

Inspection of Bread.—Two inspectors (bread experts) visit the bakeries, from day to day, and weigh the loaves. As a rule, they can draw conclusions by examining the exterior of the loaf (*i.e.* whether thoroughly baked or not). If they are in doubt whether it answers to the statutory requirement as to dry substance, they bring a loaf to the laboratory for the determination of moisture. Thanks to these intensive inspections, the delivery of short-weight loaves is becoming more and more rare.

Effect of the Orders in Council.—In every category of food the percentage of unsatisfactory samples showed a sudden increase after the respective Orders came into force, followed by a gradual decrease as the more severe requirements were complied with, except in certain cases where the figures did not take the expected course, owing to special causes. For example, the figures for jam would have shown the usual course, but for the detection, in 1929, of the use of formic acid as a preservative. This is prohibited, and 23 samples were condemned, with the result that there was a sudden increase in the percentage of adulterated samples for that year. The figures for meat are also unsatisfactory, owing to the difficulty of curing butchers of the habit of using flour and artificial colour in sausages, although the results appear more unsatisfactory than they really are, because the inspectors visit the premises of offenders more frequently than before and bring in all sausages in which they can detect any signs of adulteration.

* The Storch test is the Continental name for Dupouy's paraphenylenediamine test; *cf.* A. E. Leach, *Food Inspection and Analysis* (John Wiley & Sons, New York, 1920), p. 173.

Summary of the Principal Regulations under the Dutch Food Law

The same principle is adopted for all regulations. The name, in Dutch, under which an article is sold must be on the package, or on a shield directly above, if the article is sold loose (except in the case of certain articles sold wholesale, and for some where no misunderstanding can take place, such as sausages or bread).

The names allowed are tabulated in the regulations, and, as a rule, with a definition of the article, and with a statement of the chemical requirements, apart from the general rule that every article must conform in its properties with those described, that it must not have deteriorated, and must not contain foreign matter other than, or in greater quantity than, is expressly allowed by the regulation in question.

For goods of better quality, some subsidiary names are allowed, the use of which is protected but not obligatory. For control, the methods of analysis given in appendices to the different regulations must be used, in so far as these are sufficient for the detection of adulteration. To prevent circumvention, every regulation contains a paragraph to the effect that goods bearing a likeness to, or likely to be sold as a substitute for, those mentioned in the respective regulations are not allowed in the trade under names that do not distinctly show their character and composition. The principal articles for which standards have been fixed are summarised below in order of date. The obligatory Dutch denominations have been translated into English.

BREAD. (May 24th, 1922.)

Strict hygienic local control. The weight of a loaf is based on a minimum weight of solids (240 grms.).

White Bread.—*Solids*, 240 grms., or a multiple thereof, per loaf; *salt*, less than 2·5 per cent.; *ash other than salt*, less than 1 per cent.

Brown Bread.—*Solids*, 225 grms., or a multiple thereof, per loaf; *ash other than salt*, less than 2·4 per cent.

Rye Bread.—*Solids*, 260 grms., or a multiple thereof, per loaf; *ash other than salt*, less than 2·4 per cent.

White Milk-bread.—*Solids*, 240 grms., or a multiple thereof, per loaf; *ash other than salt*, less than 1·5 per cent.; *fat*, over 3 per cent.; *milk-fat*, over 1·6 per cent. on the solids (Kirschner value product of fat = 30; *i.e.* the product of the Kirschner value of the fat and the percentage of fat on the solids; *cf.* Leach, p. 551).

Cream-bread.—*Fat*, over 4·5 per cent.; *Reichert–Meissl value*, over 15; *Polenske value*, less than 2·2.

SUGARS AND SYRUPS. (June 6th, 1924.)

Candy (white), yellow candy, sugar (white), yellow sugar, milk-sugar, starch-sugar, starch-syrup (all with a fair allowance for ash and non-sugar, SO_2 40 mgrms. per kilo.).

Candy Syrup.—*Solids*, 80 per cent.; *ash*, 1·5 per cent.; *non-sugar*, less than 16 per cent.

Sugar Syrup.—*Solids*, 80 per cent.; *ash*, 5·0 per cent.; *non-sugar*, less than 21·6 per cent.

Household Syrup.—*Solids*, 80 per cent.; *ash*, 5·0 per cent.; about 50 per cent. *starch syrup*.

Kitchen Syrup.—*Solids*, 80 per cent.; *ash*, 4·0 per cent.; about 75 per cent. *starch syrup*.

Melado, Molasses.—No regulations as to composition, but must conform to the general regulations.

SPICES. (August 19th, 1924.)

No addition of any foreign matter is allowed (salt, colour or preservative). Chemical standards are fixed for all kinds of spices; they are well below those given by samples of the respective spices of the ordinary trade qualities.

Mustard.—*Water*, 75 per cent.; *salt* (on solids), 15 per cent.; *salt-free ash*, 8 per cent. (on solids); *sand*, 1 per cent. (on solids); *sulphate* (SO_4), 1·5 per cent. on mustard.

PRESERVED MEATS. (August 20th, 1924.)

Feder number,* 4·0 per cent.; saltpetre, 0·2 per cent. (no colouring matter).

Minced Meat, Raw Sausages, Canned Meat, Boiled Sausages.—*Starch*, 4 per cent.

Liver Sausage.—*Starch*, 4 per cent.; *boric acid*, 0·3 per cent.

MARMALADES, FRUIT JUICES, LEMONADES. (September 6th, 1924.)

Jam.—*Water*, 35 per cent.; from fruit and sugar only; small allowance for addition of other fruit than mentioned on label. There is no minimum requirement for total fruit content, but at least 75 per cent. must be of the sort indicated on the label. For pine-apple jam, cherry jam, and morella cherry jam, however, the minimum requirement is only 60 per cent.

(* The Feder number is the ratio of water to organic fat-free solids; *cf.* Leach, p. 222.)

HOUSEHOLD JAM.—*Water*, 35 per cent.; from fruit, sugar and starch syrup, artificial colour, 250 mgrms. of benzoic or salicylic acid per kilo. (large allowance for addition of other fruit).

FRUIT JELLY.—*Water*, 35 per cent.; from fruit juice (30 per cent.) and sugar only (small allowance for addition of other fruit juice).

FRUIT JUICES.—Addition of 400 mgrms. of salicylic acid or benzoic acid per kilo. and 50 mgrms. of total sulphur dioxide per kilo.

FRUIT SYRUP.—*Genuine juice*, 30 per cent.; *sugar*, 55 per cent.

ACIDULATED FRUIT ("LIMONADE") SYRUP.—*Genuine juice*, 30 per cent.; *sugar*, 55 per cent.; *essential oil, vegetable colour, citric acid*; 20 mgrms. of *sulphur dioxide* per kilo; 250 mgrms. of *salicylic* or *benzoic acid*. PINE-APPLE SYRUP must contain 15 per cent. of pine-apple juice.

ACIDULATED SYRUP.—*Sugar*, 55 per cent.; *essential oil, colouring matter, citric acid or lactic acid.*

EFFERVESCENT LEMONADE.—Lemonade syrup with water and carbonic acid, *sugar*, 8 per cent.: foam stabiliser allowed, but no saponin.

TAPESTRY. (October 29th, 1924.)

Arsenic, not to exceed 100 mgrms. per sq. metre.

WALLPAPER.

Arsenic, not to exceed 5 mgrms. per sq. metre.

MEAT EXTRACTS. (November 23rd, 1924.)

Salt and spice are the only additions allowed.

(SOLID) EXTRACT OF BEEF.—*Water*, 20 per cent.; *creatinine*, 6 per cent. of solids.

LIQUID EXTRACT OF BEEF.—*Water*, 68 per cent.; *creatinine*, 1·5 per cent. of solids.

BEEF-TEA.—*Water*, 85 per cent.; *creatinine*, 1·5 per cent. of solids.

CUBES.—*Salt*, 65 per cent.; *creatinine*, 0·5 per cent. of solids.

FLOUR AND STARCH PRODUCTS. (December 20th, 1924.)

Artificial colour, bleaching agents, baking powders (no alum) allowed. Chemical standards well below numbers for current trade qualities. The following come within the regulation: All kinds of flour, flakes, starch, malted meal, dextrinised and treated flour, custards, pudding jellies, macaroni, etc. The preface "egg" is allowed for products containing 55 grms. of egg yolk or 150 grms. of whole eggs per kilo.

COFFEE, TEA AND THEIR SUBSTITUTES. (February 3rd, 1925.)

The lowest standards occurring normally in trade qualities.

CAFFEINE-FREE COFFEE.—*Caffeine*, 0·1 per cent.

COFFEE-EXTRACT.—*Solids* (non-sugar), 6 per cent.; *caffeine*, 2·5 per cent. on solids (non-sugar).

PAPER. (April 1st, 1925.)

A quire has been fixed at 25 sheets, a ream at 20 quires. Standards for quality have been fixed, giving a right to the use of special watermarks, numbers and letters.

HONEY AND HONEY SUBSTITUTES. (August 28th, 1925.)

HONEY.—*Solids* (natural), 75 per cent.; *sucrose content*, less than 5 per cent.; absence of oxymethylfurfural; *acidity*, 5 c.c. of *N* acid per 100 grms.; presence of diastatic enzymes.

HEATED HONEY.—The same, except for absence of diastatic enzymes.

ARTIFICIAL HONEY.—*Solids*, 75 per cent.; *ash*, 0·5 per cent.

MILK AND PRODUCTS FROM MILK. (October 7th, 1925.)

System of licensed retailers; high hygienic requirements locally.

MILK.—*Freezing-point*, −0·53°; sp. gr. of *serum*, 1·0240 at 15·0°/15·0° C.; *refraction*, 1·3420 at 17·5° C.; *acidity*, 9·0; no dirt; no streptococci.

PASTEURISED MILK.—The same; no *B. coli*; *bacteria*, not more than 25,000 per c.c.

SEPARATED MILK.—The same, except for *fat*, less than 1 per cent.

CREAM.—*Fat*, over 20 per cent.

WHIPPED CREAM.—*Fat*, over 40 per cent.

BUTTER-MILK.—*Solids-not-fat*, above 7·3 per cent.; *milk sugar*, above 3 per cent.; *acidity*, equivalent to 20 to 40 c.c. of 0·25 *N* alkali per 100 c.c.

COCOA AND CHOCOLATES. (January 1st, 1926.)

COCOA POWDER.—*Fat*, over 22 per cent. (on solids); *shell*, less than 4 per cent. on solids-not-fat; *water*, less than 9 per cent.; *ash*, less than 14 per cent. (on solids-not-fat).

SECOND-GRADE COCOA POWDER.—*Fat*, 15 to 22 per cent.

CHOCOLATE.—*Cocoa, sugar*, necessary additions for flavour and taste; *cocoa content*, 32 per cent.

MILK CHOCOLATE.—*Cocoa content*, 25 per cent.; *milk solids*, 12·5 per cent.

MARGARINE. (February 1st, 1926.)

MARGARINE.—*Salt, ad lib.*; *water*, less than 16 per cent.; *fat*, over 80 per cent.; *benzoic acid*, less than 0·2 per cent.

MARGARINE MIXTURE.—The same, with 15 per cent. of genuine butter (Kirschner value, 3·0).

DETERGENTS. (February 5th, 1926.)

Soft soap fatty acids, 38 per cent.; hard soap I, 60 per cent.; hard soap II, 40 per cent.; hard soap III, below 40 per cent.; soap-flakes, 80 per cent. of fatty acids; all these with small allowance for alkali carbonate and hydroxide.

SODA CRYSTALS.—36 per cent. of *Soda ash*, and 95 per cent. of Na_2CO_3.

BLEACHING POWDER.—*Active chlorine*, 25 per cent.

SOAP-POWDER I.—*Fatty acids*, 35 per cent.

SOAP-POWDER II.—*Fatty acids*, 30 per cent.

WASHING POWDER.—*Fatty acids*: 10 to 25 per cent.; declaration of percentage of fatty acids on package obligatory. *Oxidising Agent and Water-glass* allowed with declaration.

BEER. (November 1st, 1926.)

Original wort, 9 per cent. *Ratio of extract to alcohol*, 0·8–2·5; *saccharin*, 1·5 grm. per *hl.*; *caramel; sulphur dioxide*: 25 mgrms. per litre.

VINEGAR. (January 1st, 1927.)

VINEGAR.—*Acetic acid*, 4 per cent.; additions of salt and caramel allowed.

DOUBLE VINEGAR.—*Acetic acid*, 8 per cent.

VINEGAR WITH INDICATION OF ORIGIN (*e.g.* beer-vinegar, malt-vinegar, raisin-vinegar).—*Acetic acid*, 4 per cent. by fermentation only; *solids other than salts*, more than 0·7 per cent.

WINE VINEGAR.—The same, except for *acetic acid*, 5·5 per cent.

SPIRIT VINEGAR.—The same, except for *acetic acid*, 8·0 per cent.

SOLUTION OF ACETIC ACID.—*Acetic acid*, 12·5 to 80 per cent.

ACETIC ACID ESSENCE.—*Acetic acid*, 80 per cent.

OILS AND FATS. (April 1st, 1927.)

These must be free from water; *acidity*, equivalent to less than 8 c.c. of *N* alkali per 100 grms. When sold without indication of origin, artificial colour is allowed; with indication of origin (*e.g.* beef-fat, olive oil), no colouring allowed. The use of inedible fat in factories is subject to special supervision.

CHEESE. (July 1st, 1928.)

Every cheese must bear a mark indicating its fat content (on solids):

LEAN, "MAGER."—Below 20 per cent.

20+	Between 20 per cent. and 30 per cent.
30+	Between 30 per cent. and 40 per cent.
40+	Between 40 per cent. and 48 per cent.

V.V. OR VOLVET.—Over 48 per cent.

R 65.—Over 65 per cent. (cheese made from cream).

ICE CREAM. (August 16th, 1929.)

MILK ICE.—There is a system of licensed producers and retailers. Strict hygienic control. Storch reaction negative; bacterial count, 100,000; *B. coli*, negative; artificial colour allowed.

ICE CREAM.—The same, with 12 per cent. of *milk-fat*.

WINE AND CIDER. (January 1st, 1930.)

WINE.—Every wine must have the composition, colour, odour and taste, characteristic of the sort for which it is offered (Art. 7). When an origin is expressly mentioned, the wine must conform to the standards prevailing in trade for this sort of wine of the mentioned origin (Art. 8). *Potassium sulphate*, 2 grms. per litre; *sulphur dioxide* (total), 450 mgrms., (free) 45 mgrms. per litre.

FRUIT WINE (CIDER).—*Fruit juice*, 30 per cent.; *benzoic acid*, 300 mgrms. per litre; or *sulphur dioxide* (total), 200 mgrms., (free) 20 mgrms. per litre; *caramel*, *amaranth*, and *ponceau* permitted.

KAPOK. (July 1st, 1930.)

Java kapok must be genuine and labelled. Kapok mixtures with other fibres must be labelled and percentages given correctly.

EGGS. (September 1st, 1931.)

Definitions of different qualities of eggs are given in accordance with recognised trade standards.

Eggs of all sorts must be marked to indicate the quality, with the exception of genuine fresh eggs, on which a mark to this effect is permissible, but not obligatory.

FRESH EGGS.—Eggs which have not been submitted to any means of preservation. No marking necessary.

"Foreign fresh eggs" must be sold under this designation.

COLD-STORAGE EGGS.—Eggs which have been kept at any time in cold storage.

PRESERVED EGGS.—Eggs which have been treated with lime, silicate, or the like.

SECOND-GRADE EGGS.—All other hens' eggs fit for consumption.

KEURINGSDIENST VAN WAREN,
KEIZERSGRACHT, 732–734, AMSTERDAM.

The Analysis of Cadmium Red Pigments

BY CHARLES GASPARD DAUBNEY, M.Sc., A.I.C.

CADMIUM red is usually a mixture of cadmium selenide, cadmium sulphide and barium sulphate. In spite of its comparatively simple composition, considerable difficulty has been experienced in the analysis of samples of this material. An investigation of the methods of analysis available was consequently undertaken.

Previous to the work to be described, the method employed was as follows:

(1) Extraction of the material with nitric acid, until free from colour, diluting with water, and filtering off the insoluble barium sulphate.

(2) Adding hydrochloric acid and potassium chloride to the filtrate, boiling, and precipitating the selenium with sulphur dioxide.

(3) Passing hydrogen sulphide into the filtrate to precipitate cadmium sulphide, and converting the sulphide into sulphate.

When this procedure was used it was found (*a*) that the results for selenium were variable; (*b*) that the analytical figures always added up to less than 100 per cent.

The discrepancies indicated the unsatisfactory nature of the method of determining selenium, and suggested that the extraction of the original pigment might be incomplete. Further, it was felt that the process of determining cadmium, although the accepted method, left something to be desired.

As a standard for testing the accuracy of the various processes involved, the possibility of compounding a cadmium red of known composition was considered. As it was difficult to obtain pure cadmium selenide, pure cadmium selenate was prepared and employed as a standard source of cadmium and selenium.

PREPARATION OF CADMIUM SELENATE.—Ten grms. of cadmium carbonate were suspended in water and 13 ml. of selenic acid (Δ 1·4) were added. The mixture was warmed on a steam-bath, and, after action had ceased, the solution was filtered and concentrated in a silica dish. After cooling, the mother liquor was poured off, the crystallised cadmium selenate was dissolved in water, re-concentrated (but not sufficiently to cause crystallisation), and the aqueous solution was treated with absolute alcohol. The cadmium selenate was thrown down as a fine white powder, which was filtered off by suction, dried gently to remove alcohol, ground finely and finally dried at 105° C. until constant in weight. Van Hauer (*J. prakt. Chem.*, 1860, [1], **80**, 214) states that by drying at such a temperature $CdSeO_4,H_2O$ results. In addition to confirming the percentage of cadmium and selenium in this compound, the presence of water in the pure salt was shown qualitatively.

DETERMINATION OF SELENIUM.—Several methods were tried, including the sulphur dioxide precipitation method, which yielded variable results owing to loss of selenium, and the one adopted was that of Benesch and Erdheim (*Chem. Ztg.*, 1930, **54**, 954; ANALYST, 1931, **56**, 133), in which the selenium is precipitated with hydrazine hydrochloride. Lehner and Kao (*J. Amer. Chem. Soc.*, 1925, **47**, 769; ANALYST, 1925, **50**, 255) state that to bring down selenium in the black form leads to errors, owing to occlusion both of solid impurities and of moisture which cannot be removed at 105° C., but, under the conditions to be described, this error does not appear appreciable.

A known quantity of cadmium selenate (about 0·1 grm.) was dissolved in 400 ml. of water containing 5 ml. of concentrated hydrochloric acid, and 20 grms. of hydrazine hydrochloride were added. The liquid was slowly heated to boiling, and kept boiling for half-an-hour. The black selenium was separated on a Gooch crucible, and washed, first with water, then with alcohol, and dried to constant weight at 105° C.

Selenium taken. Grm.	Selenium recovered. Grm.
0·0289	0·0288
0·0289	0·0288

If larger quantities of selenium are present (0·08 to 0·1 grm.), needing more reagent, occlusion occurs, and, if less hydrazine is employed, incomplete precipitation results.

DETERMINATION OF CADMIUM.—The method adopted was that of Berg (*Z. anal. Chem.*, 1927, **71**, 321; ANALYST, 1927, **52**, 61), in which cadmium is precipitated as the 8-hydroxyquinoline ("oxine") complex. An advantage of using this reagent is that previous removal of selenium is unnecessary. The cadmium selenate (0·1 grm.) was dissolved in 100 ml. of water, the solution was made just

acid (not more than 1 per cent.) with acetic acid, 5 grms. of sodium acetate crystals were added, and the cadmium was precipitated with a slight excess (15 ml.) of a 2 per cent. solution of "oxine" in alcohol (indicated by the yellow colour of the supernatant liquid). The mixture was heated to incipient boiling, and the precipitate was allowed to settle, filtered off on a Gooch crucible, washed first with warm and then with cold water, and dried to constant weight at 105° C.

Cadmium taken. Grm.	Cadmium recovered. Grm.
0·0435	0·0433
0·0435	0·0440
0·0411	0·0412
0·0411	0·0412

APPLICATION OF THE METHOD TO CADMIUM RED.—In the analysis of such pigments, the initial process of rendering soluble as much of the material as possible is of great importance, and the major constituents are preferably determined on one sample of the pigment.

Undissolved Residue.—One grm. of pigment, previously proved free from heavy metals other than cadmium, is transferred to a Kjeldahl flask with 40 ml. of water, and 40 ml. of concentrated nitric acid are added very slowly, with vigorous swirling. The reaction commences before warming, with the liberation of some sulphur and selenium, and, unless heating is prolonged, some of this sulphur and selenium may not be dissolved. The liquid is boiled down to about 20 to 30 ml., when another 15 ml. of concentrated nitric acid are added, and the liquid is again concentrated to 20 to 30 ml. Water is added, and the insoluble portion is filtered off, ignited and weighed. This residue is almost invariably tinted brown, but examination has shown that the colour is due solely to minute traces of impurity. The filtrate is evaporated to dryness to remove the nitric acid, distilled water is added, and the solution is made up to 100 ml.

Selenium.—Sixty ml. of the solution, diluted to 400 ml. with water, are made just alkaline with ammonium hydroxide, acidified with 5 ml. of concentrated hydrochloric acid, and the selenium is precipitated with hydrazine hydrochloride, as described above.

Cadmium.—Twenty ml. of the solution are diluted to 100 ml. with water, made slightly turbid with sodium carbonate, and cleared with a slight excess of acetic acid before precipitating with "oxine."

Sulphur.—The filtrate from the selenium precipitate is heated to boiling, treated with barium chloride in the usual way, and the sulphate is weighed as barium sulphate.

Water-soluble Material.—Five grms. of pigment are boiled for five minutes with 200 ml. of neutral distilled water, and the liquid is diluted to 250 ml. and filtered. The first 100 ml. of the filtrate are rejected, an aliquot part of the remainder is evaporated, and the residue is dried at 105° C.

Moisture.—For the moisture content, 0·5 grm. of pigment is dried for 1 hour at 105° C.

Free Sulphur.—Free sulphur is determined by extracting 5 grms. of pigment with boiling carbon disulphide under a reflux condenser.

TYPICAL ANALYSES.—Below are given typical analyses of two grades of pigment:—

	Cadmium Red.	
	"Light." Per Cent.	"Medium." Per Cent.
Undissolved matter (barium sulphate) ..	59·9	59·5
Volatile matter	0·2	0·2
Water-soluble matter	0·2	0·1
Free sulphur	Trace	Trace
Total cadmium	[28·7]	[18·9]
Selenium, calculated as CdSe	13·1	19·0
Residual cadmium, calculated as CdS ..	27·0	21·3
Total sulphur calculated as CdS ..	[26·0]	—
	100·4	100·1

SUMMARY.—A method is described for the complete analysis of cadmium red pigments, wherein the selenium is precipitated by hydrazine hydrochloride, and the cadmium as an 8-hydroxyquinoline complex. This use of hydroxyquinoline is permissible only if other heavy metals are absent—which was found to be the case with all the samples of cadmium reds examined. As a check on the methods, analytical figures for cadmium selenate are given.

I wish to thank the Government Chemist, Sir Robert Robertson, for permission to publish this note.

GOVERNMENT LABORATORY,
LONDON.

The Determination of Unsaponifiable Matter with special Reference to Fish and Marine Animal Oils

BY E. R. BOLTON, F.I.C., M.I.CHEM.E., AND K. A. WILLIAMS, B.Sc., A.I.C.

IN describing an investigation into the halogen absorption of unsaponifiable matter which enabled us to classify the oils and fats into four groups (ANALYST, 1930, **55**, 5) we published a method for the extraction of the unsaponifiable matter by means of petroleum spirit. This method may be applied to the majority of oils and fats with highly satisfactory results, as the removal of unsaponifiable matter is usually complete in the three extractions specified and the product obtained is not contaminated with soap, fatty acids, or unsaponified oil.

It is, however, recognised that the method is not suitable, as it stands, for use with fish or marine-animal oils, as the extraction in such cases may not be complete. We have suggested that the remedy lies in increasing the number of times the saponified oil is extracted, and have ourselves obtained satisfactory results

by this means in many cases, but the extra time and manipulation involved have forced us to return to the use of ether as the extracting solvent.

The use of ether under certain conditions may lead to difficulties as great as those arising from the use of petroleum spirit, and the results obtained by its use in the past have lacked that precision and certainty which are required in analysis. This, in our opinion, has been due to the following:—

(i) Unless the conditions of the extraction are carefully controlled, three extractions with ether are not always sufficient for complete separation of the unsaponifiable matter;

(ii) The extract is invariably contaminated, to a considerable extent, with soap, which is difficult to remove completely.

A satisfactory method must, therefore, ensure that:—

(1) saponification of the oil is complete;

(2) the soap solution produced is alkaline, liquid, and not viscous;

(3) the proportions of soap, water and alcohol in this solution are such as to ensure that separation from the ether takes place quickly and completely without interference from emulsions;

(4) the proportion of ether which dissolves in the soap solution be as small as possible;

(5) the concentration of the soap and alcohol allows complete separation of the unsaponifiable matter in three extractions;

(6) the removal of soap, and products of its hydrolysis, from the ether extract be complete, or that it must be possible to determine the quantity remaining and allow for this in the weight of unsaponifiable matter obtained.

As a result of a long series of experiments we have concluded that the following conditions of experiment fulfil these requirements, and that departure from them to any material degree is liable to lead either to incomplete extraction or to contamination of the product.

METHOD OF DETERMINATION.—From 2 to 2·5 grms. of the oil are saponified by boiling under a reflux condenser with 25 c.c. of $N/2$ alcoholic potash for 1 hour. The flask is then removed from the condenser and its contents transferred to a separating funnel; the flask is washed out with 50 c.c. of water, which are added to the soap solution in the funnel. When the aqueous alcoholic soap solution has cooled somewhat it is extracted three times with 50 c.c. of methylated ether, the flask being rinsed with the ether before this is added to the contents of the separating funnel. The three extracts are combined in a second separating funnel and allowed to stand for a few minutes to enable any of the soap solution, which may have been mechanically carried over, to separate; this is drawn off, and the combined extracts are washed three times with 20 c.c. of $N/2$ aqueous sodium hydroxide solution and twice with water. In conducting the second and third washings with alkali and the two washings with water, the extract and washing solution are violently shaken. In general, emulsions will not form, although some trouble has been experienced with fats containing large proportions

of saturated acids, because of the low solubility of the sodium salts; in such cases it is preferable to wash with $N/2$ potassium hydroxide rather than with $N/2$ sodium hydroxide solution. After washing, the extract is filtered into a weighed flask; the second separating funnel and filter being carefully rinsed with ether which is added to the main extract. The ether is evaporated off, and the flask and its contents are dried for 10 minutes in a water-oven, allowed to cool, and weighed.

The contents of the flask are then dissolved in warm neutral alcohol and any fatty acid present is titrated with $N/10$ sodium hydroxide solution, using phenolphthalein as indicator. The weight of fatty acid found (calculated by means of the expression 1 c.c. of $N/10$ sodium hydroxide solution is equivalent to 0·0282 grm. of fatty acid) is deducted from the weight of crude unsaponifiable matter. The correction to be applied in this manner rarely exceeds 2 mgrms.

The quantities specified in the method must be strictly adhered to, as any material departure therefrom leads to serious difficulties.

The procedure described above has been the standard practice in this laboratory for well over a year, with entirely satisfactory results.

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Notes

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

A NEW METHOD OF PREPARING A PICROLONATE FROM A PICRATE AS A MEANS OF IDENTIFICATION

IN the course of some biochemical investigations carried out here, it became necessary, for purposes of identification, to convert indolethylamine picrate into the corresponding picrolonate. The usual methods of bringing about the interconversion by way of the hydrochloride or sulphate failed, owing to (1) the difficulty of hydrolysing the very insoluble indolethylamine picrate by means of hydrochloric or sulphuric acid, and (2) the ease with which soluble salts of indolethylamine decompose on evaporation, giving resinous products. The method used by Dudley, Rosenheim and Rosenheim (*Biochem. J.*, 1924, **18**, 1268) for converting spermine picrate into the hydrochloride, when applied to the present case, was also unsatisfactory.

The following new method of converting a picrate into a picrolonate, involving the use of nitron, and depending on the extreme insolubility of nitron picrate (1 in 250,000; *cf.* Busch and Blume, *Z. angew. Chem.*, 1908, **21**, 354; Cope and Barab, *J. Amer. Chem. Soc.*, 1917, **39**, 504) is described in the hope that it may be extended and prove useful to other workers.

A quantity of 0·35 grm. of indolethylamine picrate (m.pt. 243–244° C., with decomposition; picric acid determined by means of nitron 58·0, 58·2; calc. 58·8 per cent.) was dissolved in 250 c.c. of boiling water containing 3 c.c. of 2 N sulphuric acid, and a solution of 0·27 grm. of nitron in 4 c.c. of 5 per cent. acetic acid was added to the picrate solution previously cooled to 60° C. The mixture was cooled,

filtered from nitron picrate, and the filtrate was treated with 0·22 grm. of picrolonic acid dissolved in a little warm alcohol. After standing overnight a very small quantity of a sticky precipitate separated and was rejected. The clear liquid was concentrated *in vacuo* below 40° C. to 100 c.c. and cooled. The crystals which separated were recrystallised from hot water, giving deep yellow crystals of indolethylamine picrolonate, melting at 229–230° (decomp.). Ewins (*J. Chem. Soc.*, **1911, 99**, 270) gives 231° C. as the m.pt. of this compound. (Found by microanalysis: N = 18·8 per cent. Calc. for $C_{10}H_{12}N_2.C_{10}H_8N_4O_5.H_2O$: N = 19·0 per cent.)

We wish to express our thanks to the Medical Research Council for a grant which has enabled one of us (L. K.) to participate in this work.

LOUIS KLEIN and JOHN F. WILKINSON.

THE DEPARTMENT OF CLINICAL INVESTIGATIONS AND RESEARCH,
(THE UNIVERSITY OF MANCHESTER),
THE ROYAL INFIRMARY, MANCHESTER.

FLUORESCENCE IN RELATION TO SEWAGE

SEVERAL hundred effluents and sewages, and also sludges in various stages of digestion, have been examined in filtered ultra-violet light to determine whether there is any correlation between the fluorescence and any of the numerical results obtained by chemical analysis. The source of light used was the Hanovia quartz mercury vapour lamp, fitted with a light filter which allows only wave-lengths around 3650 Å.U. to pass.

Sewages, raw and partly treated, and effluents all give a blue fluorescence, due partly to suspended, and partly to dissolved substances. The intensity of the fluorescence is increased in alkaline solution, but practically disappears in acid solution.

The intensity of the fluorescence appears to have no connection with the oxygen absorption (4-hours' figures) of shaken samples. A comparison between the free and albuminoid ammonia figures and the intensity of the fluorescence of shaken, filtered or settled liquids, showed that there is apparently no connection between them.

A substance which is very strongly fluorescent can be extracted with ether from raw shaken sewage. It cannot be extracted with carbon tetrachloride, and it does not come over on distillation with steam. After evaporation of the ether two layers are obtained—a scum which fluoresces with a very intense reddish-yellow colour, and a liquid showing an intense reddish-blue fluorescence. The scum appears to be of a fatty nature, and is only partly saponifiable. The residue left on evaporation of the ethereal extract gives Reif's fluorescence test for creatinine, and a few chemical tests also pointed to the presence of this substance.

Titration of raw sewages in ultra-violet light, with fluorescein as a fluorescent indicator, has no advantage over the usual method of titration with methyl orange as indicator. With the capillary-strip method of Danckwortt and Pfau no zones, except a thin white fluorescent edge, were obtained. Stains produced by hydrogen sulphide on lead acetate paper appear a little darker under the lamp than in daylight.

Fresh crude sludge appears very dark under the lamp, and shows a faint greenish-grey fluorescence with a number of intensely fluorescent specks, blue, yellow and green in colour. The spots, which appear to be due to particles of fat and cellulose, gradually disappear as the digestion of the sludge proceeds, a fully digested sludge being practically free from them. Here, again, the lamp does

not offer any advantage over the usual methods for determining the stage of digestion. A fatty substance which can be extracted from dried sludge with carbon tetrachloride gives an intense yellowish-brown fluorescence under the lamp.

Further experiments are in progress on the fluorescence of the flora and fauna of the filter beds, but, so far as my experience goes, the claims made for fluorescence analysis cannot be extended to the examination of sewage.

I have to thank Mr. A. S. Miller, M.Sc., A.I.C., for suggestions in connection with this work, and Mr. A. S. Parsons, M.Inst.C.E., Borough Surveyor, for facilities for undertaking the investigation and permission to publish this note.

J. A. RADLEY.

READING CORPORATION SEWAGE DISPOSAL WORKS,
MANOR FARM, READING.

Official Appointments

THE Minister of Health has confirmed the following appointments:

ALBERT EDWARD PARKES, F.I.C., as Public Analyst for the County Borough of West Ham (January 1st, 1932).

HAROLD LOWE, M.Sc., F.I.C., as Public Analyst for the County Borough of Chester (January 5th, 1932).

Notes from the Reports of Public Analysts

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

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1931

OF the 1185 samples examined during the quarter, 57 were bought formally and 1128 informally. The 25 incorrect food samples included 19 milks, 2 of vinegar, and 1 each of ginger, brandy wine, cream ice, and sugar confectionery; there were also 6 incorrect samples of drugs.

MILK ADULTERATION AND THE FREEZING-POINT TEST.—The percentage of milk samples adulterated or below the minimum limits was 3·0 per cent., as compared with 6·8 per cent. and 4·7 per cent. for the corresponding quarters of 1929 and 1930. This may be partly due to the publicity given to a Court case in which the freezing-point method was introduced for the first time. In many cases it has been found possible to use, as a basis for calculation, the freezing-point of a farm sample taken in connection with a case, thus increasing the accuracy of the calculation. Thus, in the case referred to above, two samples were taken, respectively, from a serving can and from a churn loaded on a lorry. Both were proved to contain added water (the amount in the sample from the churn being 24 per cent.) by means of the evidence afforded by the freezing-point test and the presence of nitrates. A sample of the mixed milk taken at the vendor's farm was of very good quality, and had a normal freezing-point. A fine of £10 in respect of each sample was imposed.

EXTRA CREAM ICE.—Twelve samples of ice cream and cream ice were examined. They contained from 2 to 24 per cent. of butter fat, and, in view of there being no standard for ice cream in this country, all but one were passed as genuine. This last sample was described as "Extra Cream Ice," and contained only 2 per cent. of fat. It was returned as being falsely labelled, since 2 per cent. is the minimum amount for ice cream, and cream ice should, presumably, contain more fat than ice cream. One would expect "Extra Cream Ice" to be unusually good.

VINEGAR.—One of the 17 samples examined consisted of artificial vinegar. At present it is difficult to prosecute a vendor for the sale of artificial vinegar for vinegar, for the retailer is usually unaware of the nature of the article supplied to him in many cases as "pure vinegar," and it is almost impossible to purchase a sample as "vinegar" in course of delivery from the wholesale dealer. It is to be hoped that the Committee which is to consider food standards and definitions will make some attempt to distinguish artificial vinegar from vinegar.

MINERAL MATTER IN SUGAR CONFECTIONERY.—A sample sold under the name of "Munchies," consisted of rather expensive sweets of an unusual type. They contained an inner mass of chocolate, etc., and had an outer coating of sugar, chalk and French chalk, resembling that of a pill. The total amount of mineral matter was 10·3 per cent., including 6·3 per cent. of chalk and 3·4 per cent. of talc.

H. H. BAGNALL.

Legal Notes

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

LABELLING OF POISONS

ON November 26th, 1931, the Council of the Pharmaceutical Society sued a grocer at Brentford County Court for penalties for infringement of the Poisons and Pharmacy Act, 1908. Mr. Glyn Jones, for the plaintiffs, said that the defendant, who was not a registered chemist or druggist, admitted the sale of a bottle of Izal, which was included in the Schedule to the Poisons and Pharmacy Act, 1908, as a poison. A compound containing less than 3 per cent. of homologues of carbolic acid might be sold by grocers, but if it contained more than that quantity it could not be sold unless it was described as being sold for special purposes. In this case it was described as a sheep wash, and for agricultural and horticultural purposes, and for disinfecting utensils, and was properly labelled "poison." The question was whether this was a preparation sold as sheep wash only, or for purposes in agriculture, and bearing a label, giving notice that it was sold for the special purposes for which it was produced. The Society contended that this was an attempt to convert what was essentially prohibition into encouraging the sale of a poison by other than qualified druggists. The manufacturers had suggested that this case should be tested in a friendly spirit. They put up Izal in two bottles, one for pharmacy and the other for general use, but the bottles were similar and could not be distinguished at a distance. The contents were the same, and that labelled for agricultural purposes could be sold anywhere. In his (counsel's) opinion, a sale for general purposes in agriculture was wrong, and the compound could only be sold for special purposes, which must be disclosed on the label.

Mr. C. E. Corfield, B.Sc., F.I.C., said that he had analysed the contents of the bottle in question, and that it contained 39·1 per cent. of phenols, and not less than

30 per cent. of the homologues of carbolic acid. He had also analysed the contents of one of the tins sold by grocers, and they had the same composition as the contents of the bottles.

Dr. Bernard Dyer, F.I.C., said that compounds other than Izal were used in agriculture, and that the label on every bottle must specify the method of use approved by the Minister of Agriculture. That did not appear on the bottle in question. As a soil disinfectant it would be of little use, and, if applied to a shrub or tree in leaf, according to the proportions given, it would be injurious; if used in the winter it would not be strong enough. The use of phenol preparations for soil sterilisation had now been mainly substituted by that of formaldehyde. It would make a good sheep dip if about twenty-five bottles were used to an ordinary "bath," and it might be useful on poultry farms for disinfecting hen roosts, etc. For ordinary disinfectant purposes it would be excellent. Mr. T. Tickle, B.Sc., F.I.C., agreed with the evidence of Dr. Dyer.

Mr. Norman Birkett, K.C., for the defence, said that the defendant's reply to the charge was that what he did came within the exceptions to the Act of 1908. To come within those exceptions a compound must be labelled "poison," must be in a closed vessel, and must bear the name of the maker. All these were complied with, but it was claimed that the label did not specify the special purposes for which the preparation could be used. If it were sold as a sheep wash and a farmer used it for other purposes, the vendor could not be to blame. As to the public point of view, if the contents of the bottle were diluted to 3 per cent. of the homologues of phenol it might be sold by a grocer, and the public, thinking that it was then the same article as sold by a druggist, would be deceived.

Mr. Glyn Jones, replying, said that ever since 1868 the legislature had required that poisons as a class must be sold only by qualified persons, and it was not intended that goods just on one side of the line should be sold as non-poisonous by the use of a label. Could a poison be less a poison because the packet bore the words: "It could be used as sheep wash"? The Schedule should not be evaded in that way. There must be a statement on the label that the bottle was sold for special use, and not for general use, and there was no evidence that the defendant sold agricultural or horticultural goods.

His Honour, Judge Higgins, said that the Act exempted preparations for sheep wash and for purposes of agriculture and horticulture, and he thought that the label covered the sale in this case. It was quite clear that agricultural and horticultural purposes included the washing of pans, disinfecting of premises, and cleansing of vessels, all of which must form part of agricultural work. He thought the Act had omitted something. It should have added the words: "It must not be used for any other purpose than those specially stated."

Judgment was given for the defendant, with costs.

General Medical Council

PHARMACOPOEIA COMMISSION

REPORTS OF SUB-COMMITTEES*

In addition to the Reports of the Pharmaceutical Chemistry Sub-Committee and of the Cod-liver Oil Colour Test Sub-Committee (*cf.* ANALYST, **1931**, **56**, **457**), the following Reports have been issued:

* The Reports may be obtained from the General Medical Council, 44, Hallam Street, London, W.1. Prices: No. 1, 1s.; Nos. 2 and 3 together, 3s.; No. 4, 1s. 6d.; No. 5, 1s.; No. 6, 1s. 6d.; No. 7, 1s.; No. 8, 1s. 6d. Criticism of the recommendations is invited.

REPORT OF PHARMACY SUB-COMMITTEE, AUGUST, 1930. (No. 1.)

This Sub-Committee suggests new formulae for certain preparations to be added to the Pharmacopoeia, and makes recommendations relating to the manufacture of some which require alteration. The subjects dealt with include Acids, Alcohol, Confections, Effervescing Preparations, Extracts and Liquid Extracts, Glycerins, Infusions, Liniments, Lozenges, Mucilages, Ointments, Oxymels, Plasters, Powders, Resins, Solutions, Spirits, Suppositories, Syrups, Vinegars, Waters (Aromatic), and Miscellaneous Preparations. The Sub-Committee recommends that Industrial Methylated Spirit should be described in the Pharmacopoeia, and that, subject to the statutory regulations, its use in making solid extracts and certain other preparations should be permitted.

REPORT OF THE SUB-COMMITTEE ON DIGITALIS AND STROPHANTHUS, MAY, 1931. (No. 4.)

The Sub-Committee makes recommendations for the preparation of tincture and infusion of digitalis and of tincture of strophanthus, and puts forward proposals for the biological standardisation of these drugs. Comment is invited on these proposals.

REPORT OF THE SUB-COMMITTEE ON THE PREPARATION OF STERILE SOLUTIONS FOR INJECTION, 4TH MAY, 1931. (No. 5.)

The Sub-Committee was appointed to prepare for the Commission a general statement of the principles to be adopted in sterilising solutions, and to supply notes on the best methods of sterilising the solutions of special drugs, which could be appended to the monographs on these drugs in the Pharmacopoeia. The recommendations cover the sterilisation of glass vessels and containers, heating in an autoclave, Tyndallisation, filtration, sterilisation of oily solutions, and an emergency method of sterilisation. The methods most suitable for certain specific drugs are given. The report deals also with the preparation of sterilised distilled water and of physiological saline solution.

SECOND REPORT OF PHARMACY SUB-COMMITTEE, MAY, 1931. (No. 6.)

This Report presents a résumé of the Sub-Committee's recommendations on the preparation of the following articles for inclusion in the new Pharmacopoeia:—Collodion, Elixir Cascarae Sagradae, Liquid Extract of Liver, Dry Extract of Liver, Dry Extract of Hyoscyamus, Eye Ointments, Hydrargyrum *cum* Creta, Concentrated Infusions, Injections, Liniments, Oxymels, Pills, Powders (for which a system of description based on coarseness or fineness is proposed), Solutions, Spirit of Nitrous Ether, Suppositories, Syrups, and Tincture of Stramonium.

REPORT OF SUB-COMMITTEE ON AMPOULE GLASS, JUNE, 1931. (No. 7.)

Glass containers of medicinal solutions should yield but little alkali to the solutions contained in them, and two tests are recommended for determining the limit of alkalinity. (1) *Applied to the glass when crushed.*—The apparatus to be used is first tested by placing the test solution (100 ml. of water, 0·4 ml. of 0·01 *N* hydrochloric acid, and 0·4 ml. of a strong solution of methyl red, made by dissolving 0·04 grm. of methyl red in 50 ml. of 95 per cent. alcohol, adding 1·5 ml. of 0·05 *N* sodium hydroxide solution and water to 100 ml.) in a vessel of resistant glass, transferring the solution, while boiling, to a 250 c.c. conical flask of resistant glass fitted with a reflux condenser, or with a simple condensing apparatus made by fitting a short wide tube of resistant glass (closed at one end and supplied with a flow of cold water) into the stopper of the conical flask. The whole is placed in a boiling water-bath, and at the end of 1 hour the red colour of the test solution should remain unaltered; otherwise, the flask and condenser are unsuitable for the test. Five grms. of the ground glass (particles passing a No. 25,

but not a No. 36 sieve) are washed free from dust with 95 per cent. alcohol in a small conical flask, and dried at 100° C., and 100 ml. of fresh test solution are added, the condenser is inserted and the contents of the flask are boiled for half-an-hour, when the colour should not have changed from pink to the full yellow of methyl red, as indicated by comparison with a solution prepared by adding to 10 ml. of the test solution 0·1 ml. of 0·1 *N* sodium hydroxide. (2) *Ampoules.*—Not less than 6 ampoules are filled to their prescribed capacity with acid solution of methyl red (8·3 ml. of 0·02 *N* hydrochloric acid and 20 ml. of strong solution of methyl red as above, made up to 1000 ml.) sealed and heated in steam at a pressure of 15 lbs. per sq. in. for half-an-hour. After cooling, the pink colour should show no change on comparison as described above. The tests should, if possible, be carried out not more than 14 days before the ampoule is to be used, and, if stored ampoules do not respond to the test, they should be re-tested after washing internally with a 5 per cent. (v/v) solution of acetic acid, followed by 3 washings with water, provided that, if the ampoules then pass the test, this washing is carried out before they are brought into use.

D. G. H.

REPORT OF SUB-COMMITTEE ON ERGOT, OCTOBER, 1931. (No. 8.)

The conclusions reached by the Sub-Committee are that ergotoxine is to be regarded as the active principle for which ergot preparations are administered; that the colorimetric method carried out as recommended permits of an accurate determation of total alkaloid in ergot, and its liquid extract; that the colorimetric method has advantages over gravimetric methods in requiring smaller amounts of material and less time; and that the margin of error in biological methods is at least as great as that due to the variation in the relative proportion of ergotoxine and ergotinine in the total alkaloid. Since the variation in the alkaloidal content of ergot of rye is wide, the standard for the alkaloid in the liquid extract is important, and it is recommended that it should be 0·05 per cent. of total alkaloid ±0·01. The strength of the official extract is recommended as corresponding with 0·03 per cent. of ergotoxine, and, since the evidence before the Sub-Committee suggests that 60 to 70 per cent. of the total alkaloid consists of ergotoxine, this percentage is equivalent to a total alkaloid percentage of 0·05, measured by the colour test. The M. I. Smith colour test for ergot is capable, particularly in its slightly modified form, of giving results which agree closely in the hands of different workers. The ether must be free from peroxide; and, although hydrochloric acid may be used instead of sulphuric acid, traces of peroxide affect the test to a greater extent, and the sulphuric acid method is recommended for official adoption.

Sulphuric Acid Method.—Five grms. of ergot, in No. 60 powder, are extracted with cold petroleum spirit (b.pt. 40–50° C.), and, when the fat is completely removed, the extracted drug is dried at a temperature not exceeding 30° C., and 100 ml. of anaesthetic ether are added. After standing in a stoppered glass for 10 minutes, 0·5 grm. of light magnesium oxide, diffused in 20 ml. of water, is added, and the mixture is shaken at intervals during 30 minutes. Powdered tragacanth (1·5 grm.) is then put in, and, after shaking, 50 ml. (2·5 grms. of drug) are filtered through cotton wool, and shaken in a separator with 4 successive 10-ml. portions of a 1 per cent. (w/v) solution of tartaric acid in water. The aqueous liquids are separated and mixed, the dissolved ether is evaporated, and water is added to suitable volume (say, 40 ml.), and to 2 ml. of this solution is added with constant shaking, and drop by drop, with cooling arrangements, 1 ml. of a solution of dimethylamino-benzaldehyde (0·25 per cent., w/v, in sulphuric acid). The mixture is exposed to bright light until the blue-violet coloration reaches a maximum. A standard for comparison is made at the same time and in the same way by adding to 2 ml. of a freshly-prepared 0·006 per cent. (w/v) solution of ergotoxine ethane sulphonate in 1 per cent., w/v, tartaric acid, 1 ml. of solution

of dimethyl-amino-benzaldehyde. Quantities are so arranged that the acid solution of alkaloids is diluted to produce a colour very close to that of the standard. The proportional intensities allow of the calculation of the amount of alkaloid. If the liquid extract of ergot is to be assayed, 5 ml. are treated with 50 ml. of water, rendered slightly alkaline with ammonia, and extracted with 40, 25, 20 and 10 ml., successively, of anaesthetic ether, the united extracts are washed with 25 ml. of water mixed with 0·2 ml. of dilute ammonia and then with 25 ml. of water, and the treatment with tartaric acid is carried out as above.

The Hydrochloric Acid Method.—This needs no precautions as to heat. To 5 ml. of liquid extract are added 20 ml. of a 1 per cent. (w./v.) solution of sodium bicarbonate (the mixture should be alkaline to litmus), and the mixture is extracted with 40, 25 and 15 ml. of anaesthetic ether. The united extracts are washed with 10 ml. of a 1 per cent. solution of sodium bicarbonate, and the ethereal solution is extracted with 15 ml. of a 1 per cent. (w/v) solution of tartaric acid. The acid layer is drawn off, and the extraction is repeated twice with 10 ml. of acid. The dissolved ether is removed from the united acid liquids, which are made up to a suitable volume, and the colour test is applied as before, the hydrochloric acid reagent being used.

D. G. H.

Dominion of Canada

REPORT OF THE DOMINION CHEMIST FOR THE YEAR ENDING MARCH 31ST, 1930

IN his Annual Report, Dr. F. T. Shutt points out that, as in the past, the work of the Division of Chemistry of the Department of Agriculture has been carried forward with two main functions in view: the investigation of problems affecting Canadian agriculture and the assistance of farmers, through correspondence and by analytical work, in matters related to soils, manures, feeding stuffs, well waters, etc.

In addition to these two main branches of work, the Division officially examines and reports on meat and canned foods and other packing-house products from the Health of Animals Branch; canned, preserved and fresh fruits from the Fruit Branch; condensed and evaporated milks, milk and cream powders, etc., from the Dairy and Cold Storage Branch.

Further, the division has rendered chemical assistance to the following branches of the Government service: Customs and Excise Branch, Department of National Revenue, National Parks Branch, Department of the Interior, Entomological Branch, Live Stock Branch, Seed Branch, Department of Agriculture, Department of National Defence, Public Printing and Stationery Department, Marine and Fisheries Department.

The number of classified samples received for examination during the year was 5,451, approximately 1200 more than during the preceding year. A comparison of the tables for the two past years shows that there has been an increase in every branch of the Division's activities, with the exception of well waters—the most marked increase being in the phase of work dealing with cereals, feeding stuffs and forages. The subjects specially investigated include the following *inter alia*:—

SPENT BONE CHAR.—During the past five years the spent bone char from the clarifying of raw sugar, which was formerly used solely as a phosphatic fertiliser, has been employed in stock feeding as a "mineral" adjunct to the ration to furnish lime and phosphoric acid, necessary elements for bone and tissue building in the animal. It has been further suggested that bone char, by reason of its porous

character and the presence of charcoal, may be useful in the animal economy in regulating or, perhaps, in preventing intestinal disturbances. The bone phosphate content ranges from 72 to 82 per cent., and is from 20 to 30 per cent. higher than that found in edible bone meals.

IMPORTED COLOURS FOR PEAS.—Three samples of imported colours for peas were examined. One sample was naphthol green B (S & J 398), a non-permissible coal-tar dye. The other two samples contained natural colouring matter. One of these samples—a dark green liquid—contained 0·25 per cent. of copper.

SPECIAL JAM INVESTIGATION.—With a view to the establishment of new standards for jams, several samples of strawberry, raspberry and cherry jams, and of the syrups used in their preparation were examined.

The average, maximum and minimum percentages of water-soluble solids (determined by difference) in forty-five samples of strawberry jams were 71·1, 80·3 and 64·8, respectively.

The average, maximum and minimum water-soluble solids (determined by difference) in ten samples of raspberry jam were 71·9, 76·3 and 65·8, respectively.

The average, maximum and minimum water-soluble solids (determined by difference) in eight samples of cherry jams were 73·1, 77·2 and 69·8, respectively.

A summary of results of analyses of seventeen samples of syrups used in the preparation of these jams is given in the following table:

SUMMARY OF RESULTS OF ANALYSES OF SYRUPS USED IN THE PREPARATION OF JAMS

	Total sugars. Per Cent.	Sucrose. Per Cent.	Invert sugar. Per Cent.
Average	67·1	51·1	16·0
Maximum	68·0	54·9	25·9
Minimum	66·5	40·7	12·7

Four samples of strawberries used in the preparation of strawberry jams were analysed. The results of analyses were as follows:

ANALYSES OF STRAWBERRIES USED IN THE PREPARATION OF STRAWBERRY JAMS

Variety.	Total solids. Per Cent.	Water-insoluble solids. Per Cent.	Total sugars (as invert). Per Cent.	Pectin (as calcium pectate). Per Cent.	Ash. Per Cent.	Acidity (as citric acid). Per Cent.
	9·34	2·27	3·64	1·20	0·64	1·53
Aroma ..	9·86	1·62	3·92	0·98	0·72	0·89
Aroma ..	10·26	2·31	4·34	1·34	0·62	1·08
	9·41	2·42	3·53	0·72	0·81	1·14

PRESERVATION OF EGGS WITH "DRY ICE."—It has been shown that one factor in the deterioration of eggs on storage is the loss of carbon dioxide. It therefore seemed probable that eggs would keep better if this loss of carbon dioxide was prevented by keeping the eggs in an atmosphere containing a small percentage of carbon dioxide.

In co-operation with the Poultry Division of the Livestock Branch a preliminary investigation was carried out in these laboratories to determine whether or not the storage of eggs in an atmosphere of carbon dioxide by enclosing them in sealed boxes containing "dry ice" (solid carbon dioxide) would assist in their preservation, and to ascertain how much "dry ice" would furnish the best results for keeping eggs during the summer for ten to fifteen days. The results seemed

to show that even quite small percentages of carbon dioxide influenced the keeping qualities. It was found that 30 dozen eggs, which were kept in a vaseline-sealed metal container for twelve days, showed very little visible deterioration at the end of this period. The percentages of carbon dioxide in the container at the beginning and end of the period were determined and found to be 0·05 and 0·28 per cent. by volume, respectively.

FERMENTATION IN CANADIAN HONEY.—The Canadian honey industry has suffered considerable losses through the spoilage of honey on storage by fermentation. This fermentation is caused by sugar-tolerant yeasts, several types of which have been isolated and studied by the Division of Bacteriology of the Central Experimental Farm.* Infection by these organisms may be due, in part, to careless handling, and, in part, to the transportation by the bee of yeasts from the flowers to the comb. In so far as the infection is due to careless handling it can be avoided; in so far, however, as it is due to the bees themselves it cannot be avoided, and, therefore, some control measure is necessary in order that the activity of the yeasts may be kept at a minimum.

In order to obtain an insight into the conditions most favourable to the growth of yeasts in honey the following investigation was undertaken by the Division of Chemistry in co-operation with the Divisions of Apiculture and Bacteriology. Two hundred samples of honey, collected from all parts of Canada, were sent to the Division of Apiculture. There, each sample was divided into two parts, one of which was placed in a hermetically sealed receptacle and stored at room temperature, whilst the other was sent to the Divisions of Bacteriology and Chemistry for bacteriological and chemical examination.

At the time of the publication of this Report 122 samples of the series had been analysed, and the results are summarised in the following tables:

MOISTURE, PER CENT.

	15–15·9.	16–16·9.	17–17·9.	18–18·9.	19–19·9.	20–20·9.	21–22.
Number of samples	1	19	35	50	14	2	1
Percentage of samples	1	15·0	28·5	41·0	11·0	1·5	1·0

ASH, PER CENT.

	0·02–0·039.	0·04–0·059.	0·06–0·079.	0·08–0·099.
Number of samples	19	52	20	12
Percentage of samples	16	43	16	10

	0·10–0·139.	0·14–0·199.	0·20–0·299.	0·331.
Number of samples	6	5	5	1
Percentage of samples	5	4	4	1

TITRATABLE ACIDITY.

(c.c. of *N* sodium hydroxide solution per 100 grms. of honey.)

	10–14·9.	15–19·9.	20–24·9.	25–29·9.	30–36.
Number of samples	40	47	23	4	8
Percentage of samples	33·0	38·5	19·0	3·0	6·5

HYDROGEN ION CONCENTRATION.

(Grm.-ions per litre $\times 10^{-5}$.)

	39·8.	32–16.	16–8.	8–4.	4–2.	0–2.
Number of samples	2	38	50	25	7	1
Percentage of samples	2·0	31·0	40·5	20·0	5·5	1·0

* Bull. No. 116, New Series, Dept. of Agriculture.

Nitrogen, per Cent.

	0·019.	0·020–0·024.	0·025–0·049.	0·050–0·074.
Number of samples	1	9	88	2
Percentage of samples	1·0	8·5	83·5	2·0

	0·075–0·099.	0·100–0·125.	0·156.
Number of samples	2	2	1
Percentage of samples	2·0	2·0	1·0

Invert Sugar, per Cent.

	70–71·9.	72–73·9.	74–75·9.	76–77·9.	78–79·0.
Number of samples	4	21	49	40	8
Percentage of samples	3	17	40	33	7

Sucrose, per Cent.

	0·0.	0·1–0·9.	1·0–1·9.	2·0–2·9.	3·0–3·9.
Number of samples	15·0	16	36	22	14
Percentage of samples	12	13	30	18	11

	4·0–4·9.	5·0–5·9.	6·0–6·9.	7·0–7·9.	8·0–8·9.
Number of samples	10	5	1	2	1
Percentage of samples	8	4	1	2	1

Laevulose, per cent.

	37–38·9.	39–40·0.	41–42·9.	43–44·9.	45–47.
Number of samples	7	48	52	13	2
Percentage of samples	6	39	42	11	2

Ratio of Laevulose to Dextrose.

	0·95–0·99.	1·00.	1·01–1·09.	1·10–1·19.
Number of samples	1	3	25	41
Percentage of samples	1	3	24	40

	1·20–1·29.	1·30–1·39.	1·40–1·49.	1·72.
Number of samples	22	9	1	1
Percentage of samples	21	9	1	1

Analyses of Samples of Honey which Fermented when Stored at Room Temperature

No.	Moisture. Per Cent.	Invert sugar. Per Cent.	Sucrose. Per Cent.	Laevulose. Per Cent.	Dextrose. Per Cent.	Ash. Per Cent.	Nitrogen. Per Cent.	Titratable acidity. *N* NaOH per 100 grms. honey. c.c.	*p*H.
1.	19·3	76·0	1·0	38·6	38·5	0·253	0·097	31·5	4·5
2.	20·2	74·3	1·8	40·9	34·8	0·044	0·034	15·0	3·9
3.	22·4	70·3	1·0	39·1	32·6	0·058	0·036	20·8	4·1
4.	21·6	70·3	0·0	38·4	33·2	0·075	0·086	35·4	4·1
5.	19·5	76·8	0·0	40·9	36·2	0·072	0·040	22·4	3·6
6.	19·9	76·5	1·2	40·2	36·7	0·195	0·042	22·7	3·7

ANALYSES OF SAMPLES OF HONEY IN WHICH FERMENTATION IS SUSPECTED

No.	Moisture. Per Cent.	Invert sugar. Per Cent.	Sucrose. Per Cent.	Laevulose. Per Cent.	Dextrose. Per Cent.	Ash. Per Cent.	Nitrogen. Per Cent.	Titratable acidity. *N* NaOH per 100 grms. honey. c.c.	*p*H.
1.	18·9	72·4	1·7	43·8	30·3	0·166	0·046	17·7	3·8
2.	19·3	76·2	0·0	42·0	35·6	0·039	0·048	18·8	3·0
3.	19·9	76·1	0·3	43·4	34·5	0·048	0·034	14·5	3·7

By comparing the analyses given in the tables above with the summary of the analyses of Canadian honeys given in the preceding tables it will be seen that the average moisture of the fermented samples is definitely higher than the average moisture of Canadian honeys. This substantiates the conclusion of a previous investigation, *viz.* that a high moisture content in honey is favourable to fermentation. In the case of some of the other constituents, as, for example, nitrogen, titratable acidity, and ash, there is sufficient variation from the general average to suggest that they, too, might play a part in determining the optimum conditions for fermentation. Until the investigation is completed, however, it would be dangerous to draw any definite conclusions other than those just intimated.

Palestine

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1930

THE Government Analyst (Mr. G. W. Baker, F.I.C.) reports that 6359 samples were examined, including foods, drugs, waters, minerals, and supplies under Government food contracts.

MILK.—There was a decrease in the number of prosecutions for adulterated milk (standard: fat, 3 per cent.; solids-not-fat, 8·0 per cent.), but some of this decrease is attributed to an increase in subterfuge on the part of the vendor, helped probably by the common tendency to take samples at fixed times. One difficulty is that much of the milk sold by street vendors is from individual animals and very small herds of three or four cows, or is the mixed milk of cows, goats and sheep.

SEMNEH.—A high Polenske figure is not necessarily an indication of adulteration, as it may be due to the presence of goat butter (Atkinson, ANALYST, 1928, **53**, 520). There is a Customs duty on "mixed" (adulterated) semneh, but none on pure semneh of Syrian origin, and this has involved the examination of samples from every consignment. As a sorting test in this connection use has been found for the ultra-violet lamp. Incidentally, it has been found that the yellow fluorescence of milk is, apparently, not due to the fat, as suggested by Popp (ANALYST, 1926, **51**, 540). This is being investigated further.

ALCOHOL.—The Intoxicating Liquors Ordinance, 1927–30, specifies that "Arak" is spirits made from fruit and the anise plant by distillation. Cognac includes brandy and means spirits distilled from the fermented juice of grapes. Wine means any fermented liquor made from the juice of fresh grapes. Molasses and grain alcohols pay a higher duty than other spirits. After the 1931 vintage, grape alcohol alone is to be used for the fortification of sweet wines.

The addition of sugar other than that of the grape to wine is not permitted, and, in connection with an allegation that the addition of sugar was necessary for the manufacture of sweet wine in this country, samples of grapes were submitted by the Director of Agriculture. The sugar content of the juice ranged from 21 to 33 per cent.

CRIMINAL INVESTIGATION.—*Photography of Documents, etc.*—For the routine photography of documents, labels and other exhibits up to natural size, with the minimum of trouble, a special cabinet has been constructed. An opening in the top of this cabinet takes a folding hand camera resting vertically. The object is placed upon a movable platform in the cabinet, in which electric illumination is arranged. The exposure is controlled by the light switch and averages 30 seconds.

For taking comparison photographs on one plate of firing pin impressions in brass cartridge cases, two independent sources of illumination are used, and the intensity is varied to compensate for differences in the reflecting power of the object. Backed plates are used.

X-ray photography has been found useful for examining the internal structure of bullets without mutilation of the exhibits. In one murder case the character of the nose filling of bullets, as shown by *X*-ray photography, provided important evidence (see ANALYST, 1930, **55**, 738).

POISONING CASES.—Arsenic was detected in 72 cases, mercury in 5, and strychnine in 2 cases of animal poisoning.

In the anti-locust campaign of 1930, poison bait made of bran and sodium arsenite was distributed over large areas, especially in the Beersheba district. The question then arose whether there was any danger of contamination of water supplies collected from those areas during the rainy season. Arrangements were, therefore, made for the examination of samples taken after the first heavy rains. A sample of dead locusts and débris from a poisoned area was also examined. Of the 15 samples of water examined, one contained 0·2, one 0·1, and the rest less than 0·1 part per million, while the locust débris contained 0·05 per cent. of arsenious oxide. There is no doubt that many goats were poisoned by feeding in the affected area, but no case of human poisoning from locust bait came to the notice of these Laboratories.

Arsenic Sulphide as Poison.—In cases of criminal poisoning the arsenic is more often than not given in the form of artificial sulphide, which depends for its poisonous properties upon the amount of white arsenic it contains. Several specimens examined contained about 50 per cent. of arsenious oxide. In conjunction with lime this sulphide is used to make a depilatory preparation, and for that reason, no doubt, it is often at hand when there is any poisoning to be done. It is supposed that the natural sulphides, owing to their insolubility, are comparatively non-toxic, and this is supported by tests made in these laboratories on rats.

In one case, in which the Assistant Analyst was called to give evidence, traces of sulphide of arsenic had been found in the dust in the seams of the accused's pocket and 17·37 mgrms. of arsenic were found in 1880 grms. of viscera of the deceased. Most of this arsenic was found in the liver.

Other poisons.—Mercury is often administered as the oxide, which, apparently, has other domestic uses. Datura seeds obtained from the local thorn apple are generally crushed and inserted into figs. They are used as a narcotic to facilitate robbery.

COUNTERFEIT COINS.—The present Palestine currency was introduced into circulation in November, 1927, and in January, 1928, counterfeits of the new currency were submitted to these laboratories for examination. In all, 40 coins were examined during that year, of which 34 were confirmed as counterfeit. Very few have been submitted since.

The most obvious fault in the cast coins has generally been found in the milling. There is often at one place on the circumference of the coin either a blank in the milling or file marks in place of the cast milling It is assumed that this is the place where the "tail" has been removed, and that it represents the point on the circumference where the metal entered the mould. It has been noted that the position of the orifice in the mould (as indicated on the milling) in relation to the inscription is often the same on several coins. This may, perhaps, point to a common origin.

QUESTIONED DOCUMENTS.—During 1930, documents have frequently been submitted with a request for an opinion as to the age of the writing, but, generally speaking, conditions have been unfavourable to any useful opinion being given. In one case in which two documents were alleged to have been written at the same time, it was possible to produce evidence to the contrary.

A bundle of burnt currency notes was submitted for identification. By careful treatment in a fluid medium, it was possible to effect the separation of some of the notes and to decipher parts of the inscriptions, and, in some instances, the numbers.

The examination of a rubber stamp impression on a forged passport has suggested that in this connection the detection of forgery would be greatly facilitated if every rubber stamp in use by the Government could be distinguished by a number or other mark.

HOT SPRINGS OF PALESTINE.—The hot springs at Tiberias and El Hamme are of interest. The El Hamme waters are potable and contain up to 0·7 parts of hydrogen sulphide per 100,000. The Tiberias springs are strongly saline and contain only traces of hydrogen sulphide.

The following results (parts per 100,000) were obtained:

	Tiberias main spring.	El Hamme main spring.
Chlorides (calculated as chlorine) ..	1930	40
Total solids (dried at 140° C.) ..	3220	110
Hydrogen sulphide	0·07	0·75
Temperature at spring head ..	60° C.	47° C.

Federated Malay States

ANNUAL REPORT OF THE CHIEF CHEMIST FOR THE YEAR 1930

THE chemical work for various Departments of the Federated Malay States is carried out by the Institute for Medical Research, whose Chief Chemist is Mr. R. W. Blair, F.I.C. The work for the Medical Department includes the analysis of water, milk, sewage effluents and toddy, and biochemical and toxicological examinations.

MILK.—The Sale of Food and Drugs Enactment, 1913, prescribes standards of 3·25 per cent. of fat and 8·5 per cent. of solids-not-fat. Of the 840 samples taken by the officers of the Health Branch, 13 were deficient in fat and 54 in solids-not-fat.

SEWAGE EFFLUENTS.—Most of the 93 samples examined failed to conform to the standards prescribed by the Royal Commission on sewage disposal.

DELETERIOUS DRUGS.—Eight substances supposed to contain drugs specified in the Deleterious Drugs Enactment were examined for the Police Department,

and in two of them the leaves and seeds of Indian hemp (*Cannabis indica*), known also as "ganja," were identified.

COINS AND COINING MATERIAL.—Of the 2011 exhibits in counterfeit coining cases, 1533 were counterfeit coins. Other exhibits included 11 moulds and 5 powders (plaster of Paris).

EXTRACT OF RICE POLISHINGS.—In addition to 9504 fluid ounces of the former liquid preparation, manufacture on an extended scale of the powder (acid clay) extract was commenced, and 110 kilos. were prepared.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Determination of Starch in Cereal Products, with Special Reference to Rice. E. H. Hall. (*J. Soc. Chem. Ind.*, 1931, **50**, 429T–434T.)—In this contribution to the vexed question of starch determination, the author points out that confusion has arisen owing to attempts to force a naturally occurring substance like starch into an analytical mould and to define starch arbitrarily in terms of somewhat doubtful chemical entities, such as hemicelluloses, amylopectins, and amyloses. From the starch manufacturer's standpoint, starch means all that is included in and within the envelope of the starch granule, and nothing more, the reactions towards different enzymes or dispersing agents, or the names given to the constituents, being immaterial.

Results of determinations by Ling's barley-diastase method, Davis and Daish's taka-diastase method, and the like, where it is definitely known that part of the starch granule is not included, should be returned as "amylose," as distinguished from starch. Rask's method, described by Herd and Kent-Jones (ANALYST, 1931, **56**, 184), would appear, from its very nature, to be subject to various sources of error, such as the absorption of starch from its highly colloidal hydrochloric acid dispersion by fibre, protein, etc., which are filtered off, the danger of enclosing globules of unattacked starch, and the risk of not precipitating with alcohol all that was dispersed colloidally by the acid. The view is expressed that Rask's method cannot serve as a check on the results given by other methods.

In the light of these considerations, it is shown that starch may be easily, accurately, and comparatively quickly, determined, in the case of rice, by a combination of O'Sullivan's and Brown's methods, or by a suitable modification of Brown's method alone; this modification is probably applicable also to other cereals. The procedure recommended is as follows: 2·2 grms. of rice (ground and sieved through an 80-mesh sieve) are extracted in a Soxhlet extractor with alcohol (sp. gr. 0·92) for 1 hour, the extracted rice being then transferred to a tall 250 c.c. beaker, fitted with a cover-glass, cut to accommodate a stirring rod. The volume is made up to about 70 c.c. with distilled water, and the whole is heated to boiling, and kept boiling for 2 minutes, being well stirred meanwhile to prevent bumping

and frothing. The rod is left in the beaker and the cover replaced (to prevent the starch gel from skinning over), the temperature being allowed to fall to 60° C. Five c.c. of malt extract are now added; this is made by extracting ground malt of suitable diastatic power (at least 40 to 50 Lintner) with 20 times its weight of distilled water, and filtering till crystal-bright. The contents of the beaker are now well stirred, left for 3 minutes, heated to boiling, and kept boiling for 1½ minutes, cooled somewhat and transferred to a 100 c.c. sugar flask, the volume being kept below 100 c.c. Two c.c. of a buffer solution, made by mixing 500 c.c. of *N* sodium acetate solution with 5 c.c. of glacial acetic acid, are next added; this gives the *p*H value 5·4 after addition of the malt extract. The stopper is placed loosely in the flask, which is immersed for 15 minutes in a bath maintained as nearly as possible at 57° C. The volume is made up to 100 c.c., 10 c.c. of the malt extract are added, the stopper is replaced, and the flask is left in the bath for 60 minutes. It is then withdrawn and, the stopper having been tested for looseness, heated in a boiling water-bath for 20 minutes, and afterwards placed in a cooling bath. The contents are washed into a 250-c.c. measuring flask, made up to volume, and filtered through a fluted filter large enough to receive the whole at once (Whatman No. 12 of 24 cm. diameter is suitable); filtration is very rapid. The perfectly bright filtrate is titrated against 25 c.c. of Fehling's solution according to the directions of Lane and Eynon (ANALYST, 1923, **48**, 220) (the author reads "anhydrous maltose" for "hydrated maltose" in Lane and Eynon's Table V). After deduction of a "blank" value corresponding with 15 c.c. of malt extract, the maltose found is divided by the maltose-starch factor, to convert it into starch. With rice starch, when a malt having the diastatic power 46 Lintner is used, this factor may be taken as 0·824, which agrees with Brown's figures for malt, but it may be determined readily by a determination on the carefully purified starch in question. Three determinations by this method can be made comfortably in a day by one worker. The malt extract must be used within 24 hours of its preparation; it should be kept in a stoppered flask in presence of a few drops of toluene, and the blank should be re-determined every time it is used. As the same maltose-starch factor holds for rice as for barley and malt, it is most probable that Brown's method, especially when modified as above, is of very general application.

T. H. P.

Chemical Composition of Shea Fat. S. J. Hopkins and F. G. Young. (*J. Soc. Chem. Ind.*, 1931, **50**, 389T.)—Two specimens of shea butter have been examined, one consisting of crude and the other of refined fat. The authors show that the analytical data for these fall within the usually accepted limits, and they have also examined the fatty acids and non-saponifiable fraction. Inferences are drawn regarding the composition of the fatty acids, and a hydrocarbon, apparently identical with illipene, was isolated in considerable quantities from the non-saponifiable fraction.

Composition of Cherry Gum. C. L. Butler and L. H. Cretcher. (*J. Amer. Chem. Soc.*, 1931, **53**, 4160–4167.)—The air-dried gum, which was collected at Montezuma, Indiana, from wild cherry trees, contained 10·75 per cent. of water and 1·5 of ash. Only 14·5 per cent. was soluble in water, and the methoxyl test

by the Zeisel method gave a negative result. The approximate composition of the dry gum was:—Ash, 1·3; galactose, 27·7; total pentose, 56·1; arabinose (diphenylhydrazone method), 31·6; other pentose (calculated as xylose), 24·5; and uronic acid, 10·1 per cent.; methyl pentose and mannose absent. By hydrolysis of the gum in 0·5 *N* sulphuric acid at 90° C. for 5 hours all the pentose and practically all the galactose were split from the acidic nucleus, and the acidic fraction (isolated as barium salt) had barium and aldehyde contents of a salt of an acid consisting of 2 uronic groups and 3 hexose sugar residues corresponding with mannose. Further hydrolysis of the acid of the barium salt gave another acidic fraction, which was isolated as barium salt and hydrolysed still further, and it was eventually established that the uronic acid present was glucuronic acid. The degradation products of the cherry gum, obtained by hydrolysis in acid solution, are arabinose, xylose, galactose, mannose and glucoronic acid. D. G. H.

Rapid Method for Determining Acid-Soluble Phosphoric Acid in Eggs. J. Fitelson and I. A. Gaines. (*J. Assoc. Off. Agric. Chem.*, 1931, **14**, 558–562.)—The following procedure is more rapid than, and gives results comparable with those of, Pine's method for the determination in eggs of the acid-soluble phosphoric acid (ANALYST, 1924, **49**, 531), which Pine regarded as a better index of decomposition in eggs than the ratio between inorganic and total phosphorus studied by Chapin and Powick (*J. Biol. Chem.*, 1915, **20**, 97); it is applicable more especially to dried egg-yolk.

Twelve grms. of the dried yolk (25 grms. of dried whole egg, 50 grms. of liquid whole egg, or 25 grms. of liquid yolk) are treated in an 8 oz.-centrifuge bottle with exactly 150 c.c. of freshly-made saturated picric acid solution (treated immediately before use with 0·75 c.c. of concentrated hydrochloric acid) and a pinch of solid picric acid to ensure saturation. The bottle is stoppered, shaken vigorously by hand for a few minutes, and then in a machine for 30 minutes. The whole is centrifuged and filtered through a folded filter paper (the egg material should not remain in contact with the acid solution for more than $1\frac{3}{4}$ hours, including the time required for filtration). Of the filtrate, 100 c.c. are boiled in a 300-c.c. Kjeldahl flask with 5 c.c. of concentrated sulphuric acid, 20 c.c. of concentrated nitric acid and a few glass beads, until white fumes appear. Nitric acid is added in small quantities until a practically colourless solution is obtained when the white fumes appear, the boiling being then continued for 30 minutes. The liquid is cooled, washed into a 400-c.c. beaker (the total volume being kept below 100 c.c.), treated with 10 grms. of ammonium nitrate, made alkaline to litmus with strong ammonia solution, and slightly acidified with nitric acid. After being cooled to 25 to 30° C., the liquid is stirred mechanically for at least 30 minutes with 45 c.c. of ammonium molybdate precipitant [*Methods of Analysis, A.O.A.C.*, 1925, 3, 8(*a*)]. The determination is completed in the usual manner [*ibid.*, 3, 10(*a*)]. A correction is applied to the volume of the extraction solution for the water in the egg, and the result is returned as mgrms. of P_2O_5 per 100 grms. of dry egg. T. H. P.

Detection of Added Lecithin in Chocolate Products. W. O. Winkler and J. W. Sale. (*J. Assoc. Off. Agric. Chem.*, 1931, **14**, 537–547.)—Six methods of determining lecithin in cacao products have been tried, the best results being

obtained by a modification of the tentative method given in *Methods of Analysis of the Assoc. Off. Agric. Chem.* (2nd Edition, 1925, 322), petroleum spirit and alcohol being used for the extraction.

The lecithin content of 27 samples of raw and roasted cacao beans and liquors, representing 10 varieties of beans, was found to range from 0·47 to 0·88 per cent., calculated on the fat. According to manufacturers of chocolate and distributors of lecithin, the proper amount of lecithin to add to sweet coatings is about 0·3 per cent., which is equivalent to about 1 per cent. on the fat; such a proportion can be readily detected and fairly accurately determined by the method used. No material change in the lecithin content was noted when cacao beans were roasted at temperatures and for periods of time corresponding with commercial practice.

T. H. P.

Detection of Peroxides in Ether. L. W. Green and R. E. Schoetzow. (*Amer. J. Pharm.*, 1931, **103**, 603–605.)—The chromic acid test for the detection of peroxides developed in ethers (Leffmann and Pines, ANALYST, 1930, **55**, 399) was not found to be as sensitive as the U.S.P., *X.* test, and the presence of aldehyde still further diminished its sensitivity. By using 10 c.c. of ether and shaking thoroughly, instead of pouring the reagent through the ether, the sensitivity of the chromic acid test was increased, but could not be made to equal that of the U.S.P. test. In applying that test it is desirable to avoid vigorous shaking, to observe the appearance from time to time, instead of only at the end of an hour, and to examine the contents of the cylinder vertically as well as horizontally, since the free iodine tends to leave the aqueous layer and to be dissipated in the ether on further shaking.

D. G. H.

Determination of Strychnine in Easton's Syrup. L. A. Haddock and N. Evers. (*Quart. J. Pharm.*, 1931, **4**, 314–319.)—The individual stages of Evers's method (*Yearbook Pharm.*, 1922, 409) have been examined, and the method is modified as follows:—The total alkaloids are dissolved and transferred to a separator by means of 20 c.c. and 5 c.c. portions of *N* hydrochloric acid, 25 c.c. of saturated sodium chloride solution being used for washings. This mixture is shaken for 5 minutes each time with five 25-c.c. portions of chloroform, and the combined extracts are shaken for 5 minutes with two 5-c.c. portions of a mixture of equal volumes of *N* hydrochloric acid and saturated sodium chloride solution. These washings are then shaken with 10 c.c. of chloroform, and the combined chloroform extracts are shaken, first with a mixture of 20 c.c. of water and 5 c.c. of 10 per cent. ammonia, and then with 5 c.c. of water. The chloroform solution is separated, evaporated, and, after the addition of 1 c.c. of alcohol, re-evaporated, the residue being dried at 100° C., and washed by decantation through cotton-wool with three 2 c.c. portions of a mixture (2:1) of ether and petroleum spirit saturated with strychnine. Any alkaloids on the wool are washed back into the flask with 3 c.c. of chloroform, 1 c.c. of alcohol is added, the solution is evaporated, and the strychnine is dried at 100° C. until constant in weight. If the syrup is used, 50 c.c. are taken with 50 c.c. of saturated salt solution and 5 c.c. of concentrated hydrochloric acid, and the quantities are doubled throughout. This method avoids the incomplete extraction of strychnine, which was probably balanced

in the earlier method by the presence of quinine in the residue. The maximum recorded error for 0·01 to 0·05 grm. of strychnine in the presence of 1·5 grm. of quinine is ±5 mgrms. J. G.

Biological and Spectroscopic Tests on Ergot Alkaloids, with Notes on the Maurice Smith Colour Test. F. Wokes and H. Crocker. (*Quart. J. Pharm.*, 1931, **4**, 420–443.)—The spectroscopic work was carried out with a Hilger photographic quartz (ultra-violet) spectroscope with an iron-nickel or water-immersed tungsten arc, the extinction coefficient being found by means of a Hilger–Nutting spectrophotometer; its average deviation from the mean of at least 5 readings was not greater than 0·03. Readings were taken every 3 or 10$\mu\mu$ over the whole absorption range (200 to 700$\mu\mu$) for 0·02 per cent. solutions of the alkaloids in 1 per cent. tartaric acid or in alcohol, and for the blue colour obtained in Smith's test (*U.S. Public Health Repts.*, 1930, **45**, 1466), the results being compared against biological standardisation by Clark and Broom's method (ANALYST, 1923, **48**, 498). In the Smith test 2 c.c. of the acid solution of alkaloid are layered on 2 c.c. of a 2·5 per cent. solution of *p*-dimethyl-amino-benzaldehyde in concentrated sulphuric acid, and 2 c.c. of water are then added. The layers are mixed, with the tube immersed in cold water, and the mixture is exposed for 2 hours at a distance of 15 cm. from a mercury vapour lamp, with a water-filter to eliminate heat rays, the reaction being complete when the blue colour, as evaluated in the tintometer, has ceased to increase. This test frequently gave results higher than those from the biological method; *e.g.* it indicated that ergotinine and ergotaminine are almost equal in activity to ergotoxine, though, biologically, their activities are only about one-tenth. Ergotamine has an activity by the biological method 0·8 to 0·9 that of ergotoxine. Solutions of ergotoxine, ergotamine, ergotinine and ergotaminine are all unstable and in concentrations of 0·001 per cent. all show a characteristic absorption band with a maximum at about 316$\mu\mu$, due, probably, to a common molecular grouping. Ergotinine and ergotaminine also give a secondary band (maximum at 242 $\mu\mu$), which, however, is unsuitable for quantitative differentiation of these from ergotoxine and ergotamine. Smith's reaction gave a principal band at 580$\mu\mu$, and a secondary band at 401$\mu\mu$, but neither the tintometric nor the spectrophotometric method for the measurement of colour intensity indicated that this test provides a satisfactory method of estimating physiological activity; the origin of the blue colour is not necessarily that of the 316$\mu\mu$ band. It is concluded that the spectroscope gives high results, and cannot replace the biological method for the estimation of the activity of fresh or deteriorated preparations of these alkaloids, fair agreement being obtained only with fresh and deteriorated ergotoxine ethane sulphonate. J. G.

Assay of Official Balsams. T. T. Cocking. (*Quart. J. Pharm.*, 1931, **4**, 330–334.)—Total balsamic acids are determined by saponification of 2·5 grms. of prepared storax or tolu balsam, or of the alcoholic extract from 2·5 grms. of benzoin, by 25 c.c. of boiling 0·5 *N* alcoholic potassium hydroxide solution in the usual way. The potassium salts of the balsamic and resin acids, potassium hydroxide, and aromatic and resinoid alcohols, which remain after evaporation of the alcohol, are digested with 50 c.c. of hot water, 150 c.c. of cold water being then

added to the cooled mixture, and the resin acids precipitated by the addition of 50 c.c. of a 5 per cent. solution of crystalline magnesium sulphate. The precipitate (salts of resin acids and magnesium hydroxide) is removed by filtration on a Buchner funnel and washed with a little water, the alkaline filtrate (magnesium salts of balsamic acids, aromatic alcohols, etc.) is acidified with hydrochloric acid, and the balsamic acids are extracted in ether. In order to ensure complete separation of the acids from the alkali-soluble aromatic alcohols, the ethereal solution is extracted 5 times with a 5 per cent. solution of sodium hydrogen carbonate, each separated portion being washed with a little ether. The total alkaline solutions are then acidified with hydrochloric acid and extracted with ether, and the residue is weighed after evaporation and vacuum-desiccation over sulphuric acid. Tolu and benzoin give mixtures of benzoic and cinnamic acids, but storax gives the latter only (99 per cent. purity) which may be titrated. In the case of tolu (and benzoin) difficulty may be experienced in the neutralisation of the free acids, and in the production of a uniform suspension containing their potassium salts. The balsam (2·5 grms.) is, therefore, dissolved in 15 c.c. of hot 90 per cent. alcohol, and 10 c.c. of potassium hydroxide solution (B.P.) and 50 c.c. of water are added at once, the resulting brown translucent mixture being immediately diluted with 150 c.c. of water. The magnesium sulphate solution may then be added, and after 5 minutes on the water-bath to coagulate the precipitated salts and magnesium hydroxide, the mixture is cooled and filtered, and the total balsamic acids are separated from the filtrate as described. It is suggested that these methods are preferable to, and should replace, that previously suggested (Hill and Cocking, *Chem. and Druggist*, 1912, **80**, 412, 789) for inclusion in the B.P. J. G.

Determination of Phenolphthalein in the Presence of Caffeine and Cinchona Alkaloids and Drugs containing Anthraquinone. (*Amer. J Pharm.*, 1931, **103**, 609–610.)—To 25 c.c. of water in a separating funnel is added 1 c.c. of the medicine under investigation, followed by 1 c.c. of concentrated hydrochloric acid. Three extractions, each with 50 c.c. of ether, are made, and the extracts are washed with 25 c.c. of water. The water is discarded, and the ether is evaporated in a current of air from a 400-c.c. beaker. The residue is taken up with 5 c.c. of 95 per cent. alcohol, transferred to a 100-c.c. cylinder, the beaker is washed with 25 c.c. of water and 5 c.c. of 10 per cent. ammonia, and the whole is made up to 100 c.c. and mixed. A standard containing $\frac{1}{4}$ grain of phenolphthalein per fluid oz. is made up similarly, 1 c.c. of the standard in 100 c.c. being taken for comparison. One cylinder contains 1/120th of a grain of phenolphthalein and the other an unknown quantity from the medicine. If the sample shows an appreciably darker colour than the standard, 50 c.c. (or 25 c.c.) are diluted to 100 c.c., to get a sample somewhat approximating the colour to read in the colorimeter tubes; or, if necessary, the standard is diluted. The depth of colour is then found in Schreiner tubes, graduated in mm., and the quantity of phenolphthalein is calculated. Emodin-bearing drugs, in amounts up to 15 grains per fluid oz., do not affect the analysis. D. G. H.

Syrup of Senna and the Dispensing of Syrups in Wet Bottles. T. McLachlan. (*Quart. J. Pharm.*, 1931, **4**, 461–464.)—(1) Analyses are given of seven commercial samples:—Sp. gr. (15/15° C.), 1·2278 to 1·3082; total solids, 49·8

to 68·0 per cent.; sucrose, 36·1 to 54·4 (in one case 0·4) per cent.; invert sugar, 2·1 to 9·8 (in one case, the same as above, 44·2) per cent.; senna extract, 4·0 to 14·4 per cent. The exceptional sample was probably not made from cane sugar, since the *p*H was only 4·5, and cane sugar would not be completely inverted at ordinary temperatures at this acidity, even on prolonged keeping. The present Pharmacopoeia rulings are not sufficiently rigid as regards manufacture and standardisation of the syrup, especially since the purgative action may be destroyed if the extract is heated. (2) Syrups dispensed in rinsed bottles, which have been carelessly drained, may contain 0·3 to 4·6 or 0·4 to 6·5 per cent. of added water, according to whether the bottles are still or rotated while draining, respectively. This water may prove of importance when the sugar content of a preparation is adjusted so as to prevent either crystallisation or fermentation, and 2 per cent. of added water is considered the maximum safe addition. J. G.

Procaine Borate. G. W. Collins. (*Amer. J. Pharm.*, 1931, **103**, 555–559.)—The Council on Pharmacy and Chemistry (U.S.A.) have adopted the following standards for procaine borate for inclusion in "New and Non-Official Remedies":—Formula: $C_6H_4.NH_2COO.C_2H_4.N(C_2H_5)_25HBO_2$; a borate formed by the interaction of *p*-aminobenzoyl-diethylamino-ethanol and boric acid in the same organic solvent. Procaine borate, which closely resembles procaine hydrochloride in action and can be used for the same purposes, occurs as a fine, white odourless crystalline powder, soluble in water, soluble in alcohol (about 1 : 4); insoluble in acetone, benzene, chloroform and ether. Its aqueous solution (1 in 10) is alkaline to litmus, dissociates hydrolytically, and "melts" at 163° to 166° C. After adding 25 c.c. of water to 1 grm. of the procaine borate in a separating funnel, followed by 5 c.c. of *N* sodium hydroxide solution, and extracting with 25 c.c., 20 c.c. and 10 c.c. of chloroform, successively, the oily semi-solid residue from the chloroform extract is dissolved in 25 c.c. of a 2 per cent. solution of hydrochloric acid. Portions of this solution should respond to the tests for procaine hydrochloride. On dissolving 0·1 grm. of procaine borate in 2 c.c. of methyl alcohol, adding 5 drops of sulphuric acid, and igniting, the flame shows a green outer zone. Ten c.c. portions of a solution of 0·5 grm. in 50 c.c. of water should yield no opalescence with 1 c.c. of dilute nitric acid, and 1 c.c. of silver nitrate solution; no turbidity with 1 c.c. of diluted hydrochloric acid and 1 c.c. of barium chloride solution, and no coloration or precipitate on saturation with hydrogen sulphide. The substance should pass the arsenic test, and the limit of uncombined *p*-aminobenzoyl-diethylamino-ethanol should be 2 per cent. This is determined by adding 25 c.c. of chloroform to 0·5 grm. of the borate, shaking for 5 minutes, and, after standing, filtering the liquid, washing the insoluble portion on to a filter, adding the washings to the extract, evaporating the chloroform, and drying and weighing the residue. The amount of *p*-aminobenzoyl-diethylamino-ethanol, calculated on the dried substance, should be between 50 and 52 per cent., and that of *m*-boric acid (HBO_2) between 47 and 48·5 per cent., as determined by the Gladding method of distillation and subsequent titration. D. G. H.

Corrosion of Tin Plate. Pellerin and Lasausse. (*Chimie et Ind.*, 1931, 204; *Food Manufacture*, 1931, **6**, 328–329.)—Acetic and citric acids were used alone in this investigation, in the presence and absence of air, and in the presence and

absence of common salt and phosphates. The tests were made in tin plate containers, heated in an autoclave at 112° to 115° C. It was found that oxygen favours attack by citric acid, specially at the level of the liquid. Boiled and unboiled solutions of citric acid, and also of acid and salt, were used in lacquered and unlacquered tins, and the experiments again indicated that oxygen favours the attack of tin plate by citric acid, and that salt retards solution of tin and activates that of iron, the lacquer tending to induce solution of both iron and tin. Comparative tests with acetic acid showed the same effect of oxygen, but acetic acid attacks the iron rather than the tin. The effect of the *p*H of the acid solutions on the corrosion of tin plate was studied by adding disodium phosphate to the acid solutions to give a range of *p*H 5 to 7·7. After sterilisation, the acetic solution of *p*H 6·7 to 7·7, was free from tin and iron and the metal was bright; at *p*H 5·0 there were traces of iron in the solution, and the metal was rusty in places in the unfilled area. Acetic acid, used alone, produced corrosion; citric acid by itself caused tin and iron to dissolve, the quantity of tin increasing as the *p*H rose from 5 to 7·7, and the iron increasing with change of *p*H from 7·0 to 5·0, no iron being present when the *p*H was 7·7. Acetic acid (15 grms. per litre) caused, in 5 months, blowing of all containers, which had been kept at 38° C. after sterilisation in the presence of either air or salt, and iron, but no tin was found in solution. With citric acid, about half the number of tins were "blown" under the same conditions, and all the solutions contained tin, but only traces of iron. Acetic acid, even at low concentrations, attacks iron so readily that "blowing" ensues; but, although citric acid dissolves tin, no "blowing" occurs at low concentration. Fatty acids can attack tin plate. *Pâté de fois gras* was tinned and examined for tin and iron after (*a*) 10 and (*b*) 20 months. The amounts of metal dissolved from cans with single tinning were: Tin (in mgrms. per kilo.): (*a*), 137, (*b*), 344; iron, (*a*), 54, (*b*) 68; with double tinning: Tin, (*a*), 110; (*b*), 467; iron, (*a*), 55; (*b*), 85; from lacquered cans: Tin, (*a*) 100, (*b*) 105; iron, (*a*) 55, (*b*) 152. The lacquer film probably limits the attack on tin to the small surfaces exposed by cracking of the lacquer in manufacture. A pork meat paste acted similarly. Acetic acid corrosion was typified by that produced by pickled fish, and results obtained with preserved mushrooms were similar to those for citric acid alone. A neutral product, green peas, after 18 months' storage, showed for (*a*) tin, and (*b*) iron: with single tinning, (*a*) 72 mgrms. per kilo., (*b*) 71; with double tinning, (*a*) 38, (*b*) 33; and with lacquered cans, (*a*) 23, (*b*) 48. The retarding effect of sodium phosphate on corrosion is attributed to the formation of a thin film of insoluble phosphate over the metal surface. D. G. H.

Biochemical

Effect of Diet on Manganese Content of Milk. A. R. Kemmerer and W. R. Todd. (*J. Biol. Chem.*, 1931, **94**, 317–321.)—Within the past year several workers have used milk as a manganese-low diet for studies on the rôle of this element in animal metabolism. Cow's milk is being used so extensively in these experiments that the question of the variation in the manganese content of milk becomes an important one. If the manganese content of milk is easily affected by the amount of this element in the ration, care must be used in choosing the milk

for the work. Experiments are described on the manganese content of milk from cows and goats, when given a standard ration and when given the same ration plus manganese. The results show that milk produced by cows on a normal ration contains approximately 0·03 mgrm. of manganese per litre. The manganese content of cow's milk was not increased when sufficient manganous sulphate was added to the ration to increase the manganese intake five-fold. However, the amount in the milk used cannot be ignored, because the amount may vary with the other factors, such as the individual, the breed, and the period of lactation. The manganese content of milk from goats on a normal ration is approximately 0·082 mgrm. per litre, more than twice the amount present in cow's milk. This fact is rather significant, since no such differences were observed between cow's milk and goat's milk in the case of iron and copper. The addition of manganous sulphate, in quantities sufficient to increase the manganese intake five to tenfold, increased the manganese content of goat's milk very slightly. The increase was especially noticeable during the 4th and 5th weeks on the supplemented ration. This difference may be partly due to the decrease in the milk production, because there was a definite decrease in the amount of milk produced during the latter part of the experiment. P. H. P.

Composition of Vixen Milk. E. G. Young and G. A. Grant. (*J. Biol. Chem.*, 1931, **93**, 805–810.)—Fox farming is practised extensively in certain sections of Eastern Canada, notably Prince Edward Island. Occasionally the problem arises of rearing by artificial means a litter of fox puppies deprived of their mother. The most successful way is to introduce them into a litter of kittens, from which they are almost indistinguishable. If the mother cat accepts them the growth is usually good. On artificial feeding by cow's milk the mortality is high. No analysis of the milk of the fox could be found in the literature, and it was considered of sufficient importance commercially to make one. The milk can only be obtained in the spring and, of course, from an animal that is relatively tame. A sample of milk obtained from a well-furred medium silver fox, after about 4 weeks of lactation, was of a slightly yellowish colour, of a thick, creamy consistence, and of a faint, asphalt-like odour; it settled into 3 distinct layers. The average composition of the milk of five vixens was as follows:—Water, 81·87; total solids, 18·13; proteins, 6·25; fat, 6·30; lactose, 4·56; and ash, 0·96 per cent. Calcium and phosphate comprise about 74 per cent. of the ash, but the variation is wide. With one sample a figure of 86 per cent. was obtained. A sample of colostrum was also analysed. A table shows analyses of milk of other animals. Compared with the milk of the fox, the milk of the cat is slightly lower in protein, intermediate in fat, and similar in lactose and salt content. Compared with the milk of the cow, that of the fox is distinctly different and richer in protein, fat, and calcium phosphate. It is not surprising, on this basis alone, that the fox puppy does not thrive on cow's milk. The milk of the ewe probably shows the greatest similarity. P. H. P.

Interferometric Determination of Alcohol in Blood. J. C. Bock. (*J. Biol. Chem.*, 1931, **93**, 645–655.)—A rapid and accurate method for the determination of alcohol in normal blood is presented. It has been found that the

alcohol in the blood of adults, taken before breakfast, about 12 hours after the last meal, fluctuates from 0·0015 per cent. to 0·0113 per cent., the majority of cases varying only from 0·003 to 0·005 per cent. of ethyl alcohol. The method consists in the removal of the blood proteins with a single reagent, distillation in a very simple distilling apparatus, and determination of the alcohol by means of an interferometer. Kionka (*Pharmakologische Beiträge zur Alkoholfrage*, Jena, 1927, pt. 1) used this instrument for the same purpose, but he distilled the alcohol from the whole blood *in vacuo*, and used a very complicated, costly and fragile apparatus. The Löwe-Zeiss interferometer for liquids (and gases) is an instrument which measures the *difference* of the refractive indices of two liquids or solutions; it is capable of measuring refraction differences of liquids within 2 units of the seventh decimal. The method of making interferometric measurements and the distillation apparatus devised are carefully described. The condenser tube is made of silver or copper tubing, and precautions for washing it are given. For the removal of proteins from the blood, a phosphomolybdic acid reagent was found satisfactory. It gives a coarse precipitate and ample filtrate. The composition is as follows: 12 grms. of phosphomolybdic acid and 10 grms. of sodium sulphate (crystals) are dissolved in about 600 ml. of water; 9 ml. of concentrated sulphuric acid are added, and then the solution is boiled for approximately 15 minutes. It is cooled and made up to 1 litre. For the procedure 10 ml. of blood are run slowly into a 50 ml. glass-stoppered volumetric flask, containing about 35 ml. of the phosphomolybdic acid reagent. The flask is gently agitated (not shaken), and filled to the mark with reagent. The contents are mixed, left for 10 minutes, and transferred to a 50 ml. centrifuge tube. This tube has a slightly constricted neck, and is closed with a rubber cap. It is centrifuged for about 10 minutes at high speed. The supernatant liquid is poured through a small coarse filter; 25 ml. of filtrate are transferred to the distilling flask and distilled at a moderate rate until about 20 ml. have been received in a 25 ml. volumetric flask. The contents are made up to volume, mixed, and the alcohol is determined in the interferometer. Tests were made for losses of alcohol in manipulation by comparisons of alcohol solutions of different concentrations, which had been centrifuged, filtered and distilled with those that had not. The greatest variation from the theoretical reading, the zero value, was 4 scale divisions, but 93 per cent. of the results showed readings within ± 1 of the zero value, 2 scale divisions being equivalent to 0·001 per cent. of ethanol when an 80 mm. chamber was used. Alcohol added to blood was recovered with very small errors, varying from $+0{\cdot}0005$ to $-0{\cdot}0015$ per cent. P. H. P.

Gasometric Method for the Determination of Lactic Acid in the Blood. B. F. Avery and A. B. Hastings. (*J. Biol. Chem.*, 1931, **94**, 273–280.)—A new method is described for the determination of lactic acid in the blood. Whole blood or serum is first treated by the tungstic acid method of Folin and Wu for the removal of protein. The filtrate is then treated with 14 per cent. copper sulphate solution and 14 per cent. calcium hydroxide suspension for the removal of sugar and other interfering substances. The lactic acid in the filtrate is oxidised to carbon dioxide by potassium permanganate in the Van Slyke manometric gas

apparatus (*J. Biol. Chem.*, 1927, **73**, 121), 1 molecule of lactic acid yielding 1 molecule of carbon dioxide. A table shows the results of the gasometric determination of lactic acid in lithium lactate solutions of various concentrations. Reasonably accurate determinations can be made on samples of lactic acid varying in amount from 0·045 to 0·720 mgrm. Known amounts of lithium lactate were added to blood serum, which was then subjected to the tungstic acid and to the copper sulphate and calcium hydroxide treatment. The results were within 2 per cent. of the theoretical amounts. Parallel determinations by the gasometric method and by the Friedemann and Kendall (*J. Biol. Chem.*, 1929, **82**, 23) modification of the distillation method of Friedemann, Cotonio and Shaffer (*J. Biol. Chem.*, 1927, **73**, 335; ANALYST, 1927, **52**, 418) were made on (1) standard lithium lactate solutions, (2) whole blood, (3) serum, and (4) serum to which varying amounts of lithium lactate had been added. Both methods gave essentially the same results on pure lithium lactate solutions, but the gasometric method figures on whole blood or serum were from 0·38 to 0·71μ per litre higher than those by the distillation method. The difference between the two methods is relatively constant for varying lactate concentrations, and, therefore, it is proposed that 0·5μ per litre should be subtracted from results obtained gasometrically for blood lactate concentrations. Lactate concentrations obtained in this way should be consistent with those obtained by the Friedemann, Cotonio and Shaffer method. The advantages of the gasometric method over others are the small amount of material required, the speed and simplicity of determination, and the lack of need for special apparatus other than the Van Slyke manometric gas apparatus. Its disadvantage lies in the fact that an empirical correction must be applied if results comparable with those obtained by the distillation method are desired. P. H. P.

Determination of Glycogen in Tissues. M. Sahyun. (*J. Biol. Chem.*, 1931, **93**, 227–234.)—The method of Pflüger (*Arch. ges. Physiol.*, 1904, **103**, 169) for the determination of glycogen has been modified and made available for small amounts of tissue. The suggested modifications involve (*a*) shortening of the time necessary to hydrolyse the tissue with strong alkali (30 to 40 minutes is now recommended), (*b*) facilitation of the separation of the glycogen by precipitating it in the presence of charcoal and centrifuging, (*c*) hydrolysis of the separated glycogen for a shorter time than customary (for only 2 hours with 1 *N* sulphuric acid), and (*d*) the substitution of sulphuric acid for hydrochloric acid to avoid the introduction of chlorides. For the method, 1 grm. or less of tissues, frozen in liquid air, is introduced into a 15 c.c. graduated centrifuge tube, and enough 40 per cent. potassium hydroxide is added to bring the mixture to the 5 c.c. mark. If larger amounts of tissues are obtainable, to each grm. of the tissues used in a 50 c.c. centrifuge tube, 1 c.c. of 60 per cent. potassium hydroxide solution is added, so that the final volume of the alkali mixture does not exceed 10 or 15 c.c. The tubes are covered with tinfoil, placed in a boiling water-bath for 30 or 40 minutes, and shaken thoroughly every 5 or 10 minutes. About 50 mgrms. of active charcoal are then added, and the contents are well stirred with a fine glass rod, after which twice the volume of ethyl alcohol is added to the alkali mixture, and the contents are again stirred. Any glycogen sticking to the rod is washed with as small an

amount of hot water as possible into the tube, and twice that volume of alcohol is added. The tubes are centrifuged for 10 minutes. The glycogen is adsorbed completely on the charcoal and collects at the bottom of the centrifuge tube. The alkali-alcohol supernatant liquid is discarded. Five c.c. of hot distilled water, or less, are added, and a strip of litmus paper. A few drops of 2 *N* sulphuric acid are added to turn the blue litmus paper red, and this is followed by an equal volume of acid of this concentration. The centrifuge tubes are then replaced for 2 hours in the boiling water-bath, whereupon hydrolysis is complete. The contents are neutralised with 1 *N* or 2 *N* sodium hydroxide and introduced quantitatively into volumetric flasks. The mixture is cooled, diluted to the mark, and mixed thoroughly, and samples are removed and filtered. The filtrate is clear and colourless, and ready for sugar determinations. The reducing sugar is determined by the method of Folin and Wu (*J. Biol. Chem.*, 1920, **41**, 367), and the corresponding values in terms of glycogen are obtained by multiplying the value obtained for glucose by the factor 0·927. A table shows very good results obtained for the recovery of glycogen, added to glycogen-free tissues. An experiment which shows the effect of the presence of chloride on the Folin and Wu sugar method is described. The influence of sodium sulphate (1 *N* to 0·01 *N*) on sugar determinations was investigated; no change was observed in the final blue colour for 40 minutes, except in solutions containing 1 *N* sodium sulphate. In concentrations of 0·6 *N* sodium sulphate there was a stabilisation of the final blue colour. It was, therefore, found convenient to prepare the alkaline copper reagent of Folin and Wu in 0·6 *N* sodium sulphate solution. P. H. P.

Action of Trypsin on Different Types of Wool. C. Fromageot and A. Porcherel. (*Compt. rend.*, 1931, **193**, 788.)—Samples of three types of wool, each weighing 300 mgrms., were treated for 48 hours at 37° C. with a sodium borate and soda buffer solution at *p*H=11. After being washed, they were placed in 50 c.c. of a 1 per cent. trypsin solution at 37° C. and brought to *p*H=8 by the use of a sodium borate and hydrochloric acid buffer solution. There was a steady loss in weight, continuing up to 300 hours, in each case, but the loss with the fine wool was much less than with the others.

	Mean diameter. μ	Loss in weight as per cent. of initial weight after 300 hours.
Merino, fine	20	55
Syrian, coarse	30	77
Persian, coarse	30	82

R. F. I.

Isolation of Carotene from the Suprarenal Glands. O. Bailly and R. Netter. (*Compt. rend.*, 1931, **193**, 961–963.)—Healthy ox-glands were minced and extracted twice with 75 per cent. alcohol containing 2 per cent. of acetic acid in quantities such as to yield an extract of 45 per cent. alcoholic strength, which was then filtered. The sweetbreads were minced, extracted with acetone, the solvent evaporated in a vacuum, and an extract of the dry residue in a 1 : 4 mixture of 33 per cent. potassium hydroxide solution and 95 per cent. alcohol was shaken

with petroleum spirit. The bulk of the carotene separated from the alcoholic phase after 48 hours in a vacuum, the yield being 0·1 grm. per 10 kilos. The carotene, which comes mainly from the cortical and medullary zones of the gland, appears to be identical with that from vegetable sources; it has m.pt. indefinite at 168 to 169° C. (uncorrected), and the absorption spectrum of a 0·0005 per cent. solution showed the two characteristic bands (*b* between 510 and 525$\mu\mu$, and *F* between 480 and 490$\mu\mu$). There is evidence that the alcoholic extract contains carotene (the crystallisation of which is retarded by impurities), isomerides more soluble than carotene, or a pigment which is gradually converted into it. A connection between the resistance to infection imparted by these glands and by vitamin *A* is indicated. J. G.

Carotenase. Transformation of Carotene into Vitamin *A in Vitro*. H. S. Olcott and D. C. McCann. (*J. Biol. Chem.*, 1931, **94**, 185–193.)—Recent work by various investigators has definitely established the rôle of carotene as a precursor of vitamin *A*, and it has been concluded that the conversion takes place in the liver. If an enzyme, carotenase, is responsible for this transformation, it should be possible to prepare vitamin *A* from carotene *in vitro* by incubation with whole liver or liver extracts. The authors describe a series of experiments carried out by them, with this aim in view. The presence of vitamin *A* was detected by ultra-violet absorption spectra methods, since vitamin *A* is characterised by a broad absorption band with a maximum near 328$m\mu$. The liver used was taken from vitamin *A*-free rats. The results show that carotene can be changed into vitamin *A* by incubation with fresh-liver tissue or with an aqueous extract of liver. The agent responsible for the transformation appears to be an enzyme, provisionally called carotenase, since it is destroyed by heat. The conversion of carotene into vitamin *A*, *in vivo*, and the usefulness of ultra-violet absorption spectrum methods for the detection of vitamin *A* are confirmed. It is possible that vitamin *A* is a reduced fragment of the carotene molecule, and that reduction of carotene itself creates that part of the molecule responsible for the absorption at 328$m\mu$. P. H. P.

Growth-Promoting Properties (Vitamin *B* Complex) of the Concentrated Water-Soluble Portion of Milk. G. C. Supplee, O. J. Kahlenberg and G. E. Flanigan. (*J. Biol. Chem.*, 1931, **93**, 705–725.)—Data are presented which confirm the investigations of other workers to the effect that acidified water treatment cannot always be relied upon completely to free all commercial caseins from the water-soluble growth-promoting factors. The results also indicate the possibility of a selective adsorption and retention of the different factors of the vitamin *B* complex by caseins prepared by different methods. The meagre evidence shows that further studies are needed on the biological character of caseins used in the determination of certain vitamins. Limited amounts of rice polishings, supplementing a suitable basal ration, supplied white rats with sufficient amounts of the water-soluble maintenance factors to permit of comparable assays of the growth-promoting vitamins. Assurance of the purity and suitability of particular lots of casein is pre-requisite for such determinations. The concentrated water-soluble fraction obtained from milk after the removal of the fat,

casein, albumin, and a substantial proportion of the lactose, contains a high concentration of the growth-promoting and antipellagric factors; it contains less of the antineuritic principle (vitamin *B*) than of the other growth-promoting water-soluble factors. The growth response resulting from limited amounts of this milk derivative is increased when extra vitamin *B* (as found in rice polishings) is supplied. Growths induced by the milk vitamin concentrate, either unsuppressed or resumed after suppression, concurrently prevented or alleviated the pellagric symptoms noted. Growth may take place, even though there are wide variations in the proportions of the accessory factors supplied by the water-soluble milk vitamin concentrate and rice polishings. Predictions as to the amount of any one factor required for normal development, without knowledge of the relative amount of the other factors present, are unreliable; all of the known factors must be present to some degree. The autoclaving of a water-soluble milk vitamin concentrate at 120° C. for 5 hours adversely affects its growth-promoting properties. Intensive irradiation with ultra-violet rays for a period of 10 hours has a similar effect; such treatment, however, cannot always be depended upon completely to destroy the growth-promoting factors; this irregularity is probably due primarily to the inefficiency of the irradiation technique. It is shown that accessory water-soluble factors, other than vitamins *B* and *G*, as now defined, may be required during different periods of the life cycle, particularly at, and following, the period of adolescence. Final conclusions as to the existence of such additional factors must await further knowledge of the specificity of the water-soluble factors, and of the ability of the animal to utilise such factors during the different periods of development. According to the work described, irrespective of their final identity and classification, such factors as may be concerned in the maintenance of normal development, through the periods of structural growth and adolescence and beyond, are present in the water-soluble fraction of milk; such factors are thermo-labile at the high temperatures used in the experiments. P. H. P.

Crystalline Vitamin *D*. F. A. Askew, H. M. Bruce, R. K. Callow, J. St. L. Philpot and T. A. Webster. (*Nature*, 1931, **128**, 758.)—Of the four crystalline preparations of vitamin *D* recently described, the one prepared by the authors under the name "calciferol" has been further investigated by the new method involving the preparation of crystalline esters. The product obtained by the action of 3:5-dinitrobenzoyl chloride on the crystalline material in pyridine has been separated into two esters, each of which has been repeatedly recrystallised: —*Calciferyl* 3:5-*dinitrobenzoate* forms lemon-yellow plates, melting at 145°–147° C., and having $[\alpha]^{20}_{5461}$ + 104° in acetone, $[\alpha]^{20}_{5461}$ + 68° in benzene. On hydrolysis it yields *calciferol*, with m.pt. 114·5°–117° C., $[\alpha]^{20}_{5461}$ + 119·5, $[\alpha]^{20}_{D}$ + 105° in alcohol, $[\alpha]^{20}_{5461}$ + 99°, $[\alpha]^{20}_{D}$ + 81° in acetone, antirachitic activity 40,000 International Units per mgrm.; the solution in alcohol has an intense absorption band with a maximum of $\epsilon = 46{\cdot}0$ at 265$m\mu$. *Pyrocalciferyl* 3:5-*dinitrobenzoate* forms orange prisms with m.pt. 167·5°–169·5° C., $[\alpha]^{20}_{5461}$ + 250° in benzene, yields *pyrocalciferol*, which has m.pt. 92°–94° C., $[\alpha]^{20}_{5461}$ + 608°, $[\alpha]^{20}_{D}$ + 494° in alcohol, has no antirachitic activity, but shows an absorption band with maxima of $\epsilon = 15{\cdot}7$ at 296$m\mu$, 27·1 at 284$m\mu$, and 26·1 at 274$m\mu$.

Both calciferol and pyrocalciferol have the same empirical formula as ergosterol, and the supposition that calciferol is a direct product of the irradiation of ergosterol has been confirmed by the preparation of the dinitrobenzoate directly from the undistilled crude irradiation product. D. G. H.

Dermatitis from Oranges and Lemons. S. G. Horner. (*Lancet*, 1931, **221**, 961–962.)—A dermatitis, often of a disabling degree, was found to affect a number of workers preparing oranges and lemons in the marmalade season, and the "peelers" were more affected than the workers dealing with the fruit juices, notwithstanding the fact that in the case of the former there was practically no contact with the juice. Although among "peelers" there is predisposition to injury through accidents with knives and other implements, and friction of the wrists and forearms, it seemed probable that there is a more aggressive irritant in the peel of the fruit than the citric acid of the fruit hearts, and it is suggested that the limonene present in lemon and orange oils is the irritant. If the exposed skin was oiled before beginning work, injury was very rarely sustained, owing to prevention of damage to the horn cells from immersion in water, so that these remained healthy and resisted the action of limonene and citric acid. D. G. H.

Bacteriological

Pathogenic Fungus on Wool Cloth. A. G. Gould and E. K. Carter. (*Amer. J. Hyg.*, 1931, **14**, 694.)—An old woollen jersey, saturated with stale human perspiration, was cut into a number of one-inch squares, and upon each was placed a particle of a fresh culture of *Tricophyton interdigitale*, care being taken that none of the medium itself was transferred. A particle was also placed in a sterile Petri dish. The squares of cloth and the Petri dishes were incubated, sterile water being added daily to all. At intervals over two months, inoculations were made on nutrient media from the growth itself, and also from the piece of cloth from which the growth had been removed, so far as was possible. From the growth, positive results for *T. interdigitale* only were obtained, and from the cloth almost invariably a non-pathogenic fungus developed without *T. interdigitale*.

The authors conclude that, although the pathogenic organism was alive at the end of the period, there was no evidence of development. R. F. I.

Agricultural

Determination of Plant Ash Constituents in the Presence of Silica. J. Davidson. (*J. Assoc. Off. Agric. Chem.*, 1931, **14**, 551–558.)—Wheat and rice straws, grown with and without fertilisers, have been analysed for total and acid-soluble ash, silica, phosphorus, potassium, calcium, magnesium, iron and aluminium, and manganese. When the ash of the straw was dissolved in dilute hydrochloric acid, without previous volatilisation of silica, the results of analysis were too low in every case. Digestion of the acid-insoluble residue with hydrofluoric and sulphuric acids to expel the silica, with subsequent re-solution in dilute hydrochloric acid, yielded additional quantities of the ash constituents. When the

ash was digested directly with hydrofluoric and sulphuric acids, and then dissolved in dilute hydrochloric acid, the results agreed with the sum of the respective results obtained from the solutions of the ash and the insoluble residue after digestion with hydrofluoric and sulphuric acids, except for the acid-soluble ash and silica. The exception in these cases is due to the conversion of the bases into sulphates, rendering the results for acid-soluble ash too high and those for silica too low.

Volatilisation of silica, or possibly some other procedure to prevent retention of bases by the acid-insoluble residue, is essential for the proper analysis of ash constituents of plant substances rich in silica. It is recommended that the acid-soluble ash in plant substances rich in silica be determined, as well as the total ash, when analyses of the ash constituents are omitted.

The mechanism by which a soluble portion of ash constituents is held in the acid-insoluble residue cannot be determined from the data at hand. The fact that the variations in silica content have no effect on the magnitude of the retention does not point to adsorption. On the other hand, the fact that retention tends to increase with the concentration of the acid-soluble ash constituents, is in agreement with adsorption phenomena. T. H. P.

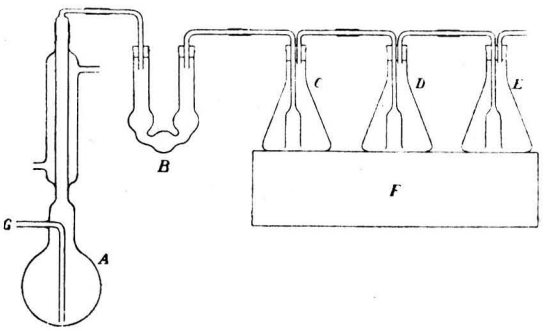
Colorimetric Methods for the Determination of Manganese in Plant Materials. J. Davidson and R. G. Capen. (*J. Assoc. Off. Agric. Chem.*, **1931, 14**, 547–551.)—Determinations of manganese in plant materials and inorganic manganese compounds have been made by the potassium periodate (*cf.* Davidson and Capen, *J. Assoc. Off. Agric. Chem.*, 1929, **12**, 310), ammonium persulphate (*cf.* Newcomb and Sankaran, ANALYST, 1929, **54**, 348), and sodium bismuthate (*cf.* Gortner and Rost, *J. Ind. Eng. Chem.*, 1912, **6**, 522) colorimetric methods, and by the gravimetric method. The first two of these methods are equally suitable for plant materials, but the sodium bismuthate method gives appreciably lower results. Ammonium persulphate is much cheaper than potassium periodate, but, when the plant materials contain an appreciable quantity of chlorides, the ash must be ignited with sulphuric acid to expel the chlorine if the persulphate method is to be used, whereas chlorides (as distinguished from hydrochloric acid) do not interfere with the periodate method. The gravimetric method is found to be inaccurate for determining manganese in plant materials. T. H. P.

Water Analysis

Determination of Organic Carbon in Sewage. E. V. Mills. (*J. Soc. Chem. Ind.*, 1931, **50**, 375–377T.)—The usual methods for the determination of organic carbon in sewage are subject to two defects: loss of organic matter in the preliminary treatment and serious lack of sensitivity. The following procedure eliminates the first source of error and results in greatly improved accuracy:

The reaction flask A is of 250 c.c. capacity and the reaction products pass through the fused-on condenser to B, which contains saturated aqueous chromium trioxide to remove oxides of sulphur, and then through C, D and E, each containing 100 c.c. of carbonate-free baryta solution (10 grms. per litre); a soda-lime tube on the gas-exit tube prevents diffusion of carbon dioxide from the atmosphere into E. The baryta flasks stand on a water-bath F.

Into A, immersed in cold water, are placed 50 c.c. of the sewage and, cautiously, 150 c.c. of concentrated sulphuric acid. Air free from carbon dioxide is passed through this mixture for 15 minutes, dissolved and inorganic carbon dioxide being thus expelled; 0·5 c.c. of saturated silver nitrate solution and 10 c.c. of saturated chromium trioxide solution are next added to the flask, which is then connected with B. The air stream is shut off by a clip at G and the contents of the reaction flask are heated by a naked Bunsen flame until a brisk evolution of gas occurs; the reaction mixture should not boil. With the proportions of water, acid and chromium trioxide given, a homogeneous mixture is formed, and excess of the



trioxide remains after the oxidation; moreover, the evolution of oxides of sulphur is minimised and such oxides should not reach the absorption flasks. The end of the absorption of carbon dioxide is shown by the settling of the precipitate and the clearing of the baryta solution in all three absorption flasks; the last of these should show little or no precipitate. The flasks are removed and allowed to cool with a soda-lime tube at each end, the contents being then filtered through a weighed Gooch crucible, on which the whole of the precipitate is thoroughly washed with boiling water; six fillings of the crucible, with slow filtration, usually suffice to remove all but traces of the baryta. The crucible is then dried and weighed, the weight being corrected in accordance with the result of a similar determination on the reagents alone. In order to correct for any small amount of oxides of sulphur which may have been absorbed, the weighed precipitate is washed with bromine water, first neutral and then acidified with hydrochloric acid. The combined washings are boiled, left for a time, and filtered, the barium sulphate formed being washed and weighed as usual. With careful working, this sulphate does not weigh more than 1 mgrm. and may, indeed, be disregarded.

The 3 : 1 acid to water ratio may be diminished somewhat if phosphorus pentoxide is mixed with the acid. By the above method, malonic acid gave 100·95 per cent. of its organic carbon as the mean of four determinations, with a maximum deviation of 0·3 from the mean, and sucrose 99·98 per cent. with maximum deviation 0·2 from the mean of three determinations. T. H. P.

Organic Analysis

Quantitative Determination of Acetic Acid in Cellulose Acetates. E. Berl, G. Rueff, W. Wahlig. (*Chem. Ztg.*, 1931, **55**, 861–862.)—The available processes are reviewed, and it is concluded that they are neither as rapid nor as

accurate as desired. In the new process proposed, which occupies an hour and a half, the cellulose acetate is hydrolysed in phosphoric acid; the acetic acid liberated is distilled in steam, and the distillate is titrated with baryta. *Apparatus.*—This consists of (*a*) a steam generator—a 1-litre flask, containing dilute baryta solution, fitted with a safety tube and a leading tube, (*b*) a distilling flask (250 c.c. capacity) fitted with a ground-glass stopper, carrying a leading tube passing nearly to the bottom of the flask, and an exit tube provided with a splash-bulb, (*c*) a long Liebig condenser, with which the exit from the splash-bulb is connected by a ground-glass joint, (*d*) a receiving flask for the distillate. *Method.*—The carefully dried sample (0·5 grm.) is introduced into the distilling flask, and 20 c.c. of phosphoric acid (89 per cent.) are added; the stopper of the flask is placed in position, and the flask is placed in boiling water and gently shaken for 15 minutes, *i.e.* until the sample has completely dissolved. Five c.c. of water are then added to the contents of the flask, from a pipette, by way of the leading tube. The flask is connected with the other parts of the apparatus, and the steam-distillation is carried out until about 450 c.c. of distillate have been collected, when the volume of liquid in the distilling flask should be from 75 to 100 c.c.; about one hour is required for the steam-distillation. The distillate is titrated with $N/5$ baryta solution, phenolphthalein being used as indicator. S. G. C.

Esters as Adulterants of Cassia Oil and their Detection. J. Callaway and T. N. Bennett. (*J. Assoc. Off. Agric. Chem.*, 1931, **14**, 571–573.)—In the U.S.P., *X.* it is specified that cinnamon or cassia oil shall contain at least 80 per cent. by volume of cinnamaldehyde, as determined by the neutral sodium sulphite method. Tests are outlined for such common adulterants as heavy metals, rosin or rosin oil, and chlorinated products, the last indicating the addition of synthetic cinnamaldehyde. In carrying out the U.S.P., *X.* assay method for cinnamaldehyde, so much 5 per cent. sodium bisulphite solution is necessary to maintain neutrality that the total volume exceeds 100 c.c.; replacement of the 5 per cent. by a saturated solution is recommended. The tests for rosin (oil) and heavy metals are fairly satisfactory with crude oils from China, but, since synthetic cinnamaldehyde free from chlorine is now available in European markets at a lower price than the oil, a more reliable test for this product is needed.

Adulteration of the oil with synthetic cinnamaldehyde would necessitate addition of non-aldehydes to render the proportion of cinnamaldehyde normal. The non-aldehyde residue (about 1·5 c.c.) remaining, after determining the cinnamaldehyde by the U.S.P. assay method, was, therefore, examined. The clear residue was heated on a boiling water-bath in a test-tube with about 3 c.c. of a 10 per cent. solution of potassium hydroxide in absolute alcohol for 2 or 3 minutes. The presence of foreign esters (other than cinnamyl acetate) was revealed by the formation of a precipitate which was usually sufficient to cause complete solidification. This test gave negative results with every one of a large number of crude oils, whereas various commercial redistilled oils yielded positive results, and the precipitates were found to contain esters of benzoic and phthalic acids. Although these acids have been reported as constituents of cassia oil, they should be dissolved in the aqueous solution, probably as sodium salts, during the treatment with the neutral sulphite, and hence should not interfere with this test. T. H. P.

Preparation and Determination of Acrolein. E. V. Zappi and R. A. Labriola. (*Anal. Asoc. Quim. Argentina*, 1930, **18**, 243–246.)—Various modifications are suggested for improving the method of preparing acrolein given by Gilman (*Organic Syntheses*, Vol. VI, 1926, 1). Acrolein exhibits great tardiness in reacting with hydroxylamine, and the method described by Sudborough and James (*Practical Organic Chemistry*, 1920, 225) for the determination of aldehydes is quite inapplicable in this case.

The method recommended is based on that of Ivanov (*Arch. Hyg.*, **73**, 307), and depends on the fixation of sodium bisulphite by the aldehyde. The solutions used are prepared by (1) dissolving 5 grms. of potassium iodide in the minimum quantity of water, adding 4·8 grms. of resublimed iodine, making up to 1000 c.c., and, after titrating with 0·1 *N* sodium thiosulphate solution, diluting with water, so that 10 c.c. of the final solution correspond with 3·49 c.c. of 0·1 *N* thiosulphate; (2) diluting 6 c.c. of commercial 30 per cent. sodium bisulphite solution to 1000 c.c. and adjusting the volume so that it corresponds with solution (1). The acrolein to be determined should be dissolved in 96 per cent. alcohol, and the solution should contain not more than 1 mgrm. per c.c. Ten c.c. of the acrolein solution, prepared by weighing, are treated with 15 c.c. of solution (2), and the whole is left in a cool dark place for 6 hours, after which the excess of bisulphite is determined by titration with the iodine solution [1 c.c. of solution (2) is equivalent to 0·001 grm. of acrolein]. Treatment of the acrolein, in chloroform or carbon tetrachloride solution, with bromine and subsequent determination of the excess of bromine, gives less accurate results than the above procedure. T. H. P.

Reduction of the Bromine Derivatives of Fatty Acids. W. Kimura. (*J. Soc. Chem. Ind., Japan*, 1931, **34**, 355B.)—The method recommended is a modification of that of Rollet. The bromide is boiled with zinc and methyl alcohol, during which 5 *N* sulphuric acid is added, drop by drop. After cooling, the methyl ester of the unsaturated fatty acids is extracted with petroleum spirit. The reduction of tetra- and hexabromides is simple, but that of the decabromide is difficult, and a low yield is obtained. R. F. I.

Inorganic Analysis

Iodimetric Determination of Ferric Iron. E. Rupp. (*Z. anal. Chem.*, 1931, **86**, 217–219.)—The method is based upon conversion of the iron into ferricyanide, and its reaction with iodide: $K_3Fe(CN)_6+KI=K_4Fe(CN)_6+I$. The solution, containing not more than 0·1 grm. of iron as ferrous or ferric iron, or both, is treated with 10 c.c. of 25 per cent. phosphoric acid, 10 per cent. ammonia, (until the reaction is distinctly alkaline), water to bring the volume to 100 c.c., and 1·5 to 2 grms. of pure potassium cyanide. The liquid is heated until the colour of the solution has just changed from brown to a clear greenish-yellow, the heating being interrupted as soon as the colour change is complete. When cold, the solution is acidified with 30 c.c. of dilute sulphuric acid and titrated with 1 per cent. permanganate solution, the resulting slight pink colour being discharged with a tiny crystal of oxalic or tartaric acid. The solution is next treated with a minimum of 0·3 grm. of potassium iodide and with zinc sulphate (2 grms.); after

3 minutes' standing, the iodine is titrated with 0·1 *N* thiosulphate solution, with starch as indicator. Three minutes after the conclusion of the titration, any after-blueing is removed by continued titration. The operation requires about 30 minutes. The method is applicable in presence of manganese, chromium, aluminium, magnesium, tin, and lead, whilst copper, cadmium, nickel, and zinc interfere. W. R. S.

Determination of Oxygen and Nitrogen in Iron and Steel by the Vacuum Fusion Method. H. C. Vacher and L. Jordan. (*Bureau of Stds. J. Research*, 1931, **7**, 375–401.)—This paper contains the results of an extended study of the vacuum-fusion method for the determination of gases in steel, and a full description of the apparatus and method now adopted at the Bureau of Standards is given. On account of the highly-specialised nature of these determinations reference to the paper for working details is essential. S. G. C.

Antipyrine as a Reagent for Cobalt. K. Woynoff. (*Chem.-Ztg.*, 1931, **55**, 914.)—Whereas the addition of antipyrine to a solution of a cobalt salt gives rise to no distinctive colour-change, it is claimed that a characteristic blue colour is produced when the mixed solution is made to dry on filter paper, and this has been made the basis of the following spot test.—A strip of filter paper is saturated with the solution to be tested, and dried (the author recommends employing an electrically-heated plate). One drop of antipyrine solution (20 per cent.) is placed on the strip, which is then dried again. The formation of a blue ring on the paper denotes the presence of cobalt. The blue ring remains stable when the strip is subsequently cooled only when there is more than 0·6 mgrm. of cobalt chloride in 1 c.c. of the test solution; with a lower concentration of cobalt, the blue ring is only visible when the strip is warm; the test fails altogether when less than 0·3 mgrm. per c.c. of cobalt chloride is present. Nickel, mercury, magnesium and the alkaline earth metals do not interfere, but iron and copper mask the test by giving a brown and a yellow colour, respectively.
S. G. C.

New Colorimetric Method for the Determination of Potassium. H. R. D. Jacobs and W. S. Hoffman. (*J. Biol. Chem.*, 1931, **93**, 685–691.)—The formation of a hitherto unmentioned, stable, coloured compound of cobalt (prepared from cobalt, choline and ferrocyanide) and its application to the microdetermination of potassium in biological fluids is described. A solution of sodium ferrocyanide added to a mixture of a cobaltous salt and choline hydrochloride in aqueous solution gives an emerald-green colour immediately. Preliminary experiments showed that the colour is sensitive to minute amounts of cobalt, choline and ferrocyanide, and that, in the presence of a given excess of choline and ferrocyanide (*vide infra*), it can be used to determine colorimetrically small variations in the concentration of cobalt. The coloured solution can be diluted with water without affecting its quality; the colour develops to maximum intensity in a few minutes and maintains this intensity for hours. The usual method for the determination of potassium in the blood and the urine depends upon the precipitation of the element as the cobaltinitrite, and the subsequent determination of one of the

constituents of the precipitate. The procedure outlined for the determination of potassium in blood, urine and ash solutions, by means of the new colour, is as follows: —The potassium is precipitated from blood serum by the method of Kramer and Tisdall (*J. Biol. Chem.*, 1921, **46**, 339). Into a 15 c.c. conical centrifuge tube, marked at 6 c.c., is pipetted 1 c.c. of serum, and 2 c.c. of Kramer and Tisdall's sodium cobaltinitrite reagent are added, slowly, with constant shaking. After 45 minutes, 2 c.c. of water are added, and the tube is centrifuged at moderate speed for 15 minutes. The tube is inverted and drained briefly, 1 c.c. of water is run down its side, it is centrifuged for 5 minutes, and again inverted, and drained. The precipitate is suspended in 2 c.c. of 70 per cent. alcohol with the aid of a stirring rod, the tube centrifuged for 5 minutes, inverted, and drained. The alcohol washing is repeated once. After it has drained, the precipitate is suspended in 1 c.c. of water. Another c.c. of water is added, and the tube is immersed, with occasional shaking, in a boiling water-bath, for 10 minutes. The precipitate dissolves to form a clear, colourless solution. A small amount of insoluble material, probably protein, does not interfere. When the tube has cooled, 1 c.c. of 1 per cent. choline hydrochloride and 1 c.c. of 2 per cent. sodium ferrocyanide are added to the solution, which is then made up to the 6 c.c. mark. The precipitation of potassium from inorganic solutions or solutions of ash is made from 2 c.c. of unknown solution with 1 c.c. of reagent. The first washing with water is omitted, and the precipitate is washed twice with 70 per cent. alcohol, as outlined for serum, and the remainder of the procedure is the same. The coloured solution formed is compared with a standard coloured solution made from 1 c.c. of standard cobalt nitrate (or sulphate), 1 c.c. of 1 per cent. choline hydrochloride, and 1 c.c. of 2 per cent. sodium ferrocyanide made up to 6 c.c. with water. The standard cobalt solution is either 0·6701 grm. of $Co(NO_3)_2.6H_2O$ or 0·6469 grm. of $CoSO_4.7H_2O$, made up to 1 litre with water. These solutions are standardised against standard potassium sulphate solution containing 0·4011 grm. of potassium sulphate per litre (equivalent to 18 mgrms. of potassium per 100 c.c.), which is treated in the manner described above. The colours are easily matched in any good colorimeter. The results of determinations of potassium in blood sera, in urine, and in inorganic solutions are given. Ammonium salts interfere with the determination, and hence fluids such as urine should first be evaporated and the residue ashed. P. H. P.

Volumetric Determination of Sulphates by the Use of Benzidine Solution. S. Snyder. (*Chemist Analyst*, 1931, **20**, VI, 8–9.)—Phosphates should first be removed by dilution of a volume of sample containing about 10 mgrms. of sulphur (as sulphate) to 50 c.c., and addition of concentrated ammonia until the liquid turns faintly pink with phenolphthalein. Ten c.c. of 5 per cent. ammonium chloride solution and 1·5 grms. of magnesium carbonate are then added, and the mixture is diluted to 100 c.c., shaken, and filtered, after 30 minutes, through a dry paper. *Inorganic sulphate.*—*N*-Hydrochloric acid is added to 5 c.c. of the filtrate containing 2 drops of a 0·04 per cent. solution of bromphenol blue in alcohol, until a yellow colour is obtained (pH 4); 2 c.c. of a filtered solution of 4 grms. of benzidine in 250 c.c. of water containing the equivalent of 50 c.c. of *N* hydrochloric acid are then added, and followed, after a few minutes, by 4 c.c. of 95 per cent.

acetone. After 10 minutes the benzidine sulphate is filtered off in a glass tube. which is 7 cm. long, and 15 mm. in diameter at the top end, and has a hole (3 mm. in diameter at the bottom), which is plugged with a filter mat. The precipitate is washed with 3 1-c.c. portions of the acetone, and the filter tube and contents are then placed in boiling water. A few drops of phenol red are added, and the solution is titrated, while hot, to a definite pink colour with 0·02 *N* sodium hydroxide solution (1 c.c.≡0·32 mgrm. S.). *Total Sulphate.*—The filtrate (5 c.c.) from the phosphate precipitate is evaporated with 1 c.c. of 3 *N* hydrochloric acid, the residue is heated on the bath for 10 minutes, and the above procedure is followed. *Ethereal Sulphate* is obtained by difference. *Total Sulphur.*—Five c.c. of the original filtrate are evaporated with 0·5 c.c. of a solution containing 20 grms. of copper nitrate and 5 grms. of potassium chlorate per 100 c.c. (Benedict), and the residue is gently ignited and then evaporated with 3 c.c. of 2 *N* hydrochloric acid. The above procedure is then followed, except that the strength of the acetone should be 50 per cent. The method is specially recommended for urine and water analyses (*cf.* Rosenheim and Drummond, ANALYST, 1914, **39**, 319). J. G.

Microchemical

Detection of Glucosides in Plant Tissues. A. Niehhammer. (*Mikrochem.*, 1931, **9**, 136–142.)—Several glucosides were identified by sublimation under reduced pressure, by observing the temperature of sublimation and the appearance, crystalline form and chemical reactions of the sublimate. There is sometimes slight decomposition on subliming, but this does not interfere with most of the tests. Sections of biological tissue, as well as the substance itself, may be used for the sublimation, which is carried out in a Klein-Werner apparatus (G. Klein, *Praktikum der Histochemie, Vienna*, 1929), heating on an oil-bath for low temperatures, and a sand-bath for high temperatures. The sublimate is collected on a small cover glass attached to the cooler with anhydrous glycerin. *Aesculin*, or a slice of the bark of horse chestnut trees containing the glucoside, or the concentrated alcoholic extract, gives a sublimate under reduced pressure at 260° C. When sublimed at 330° C. for one or two hours fine crystals are formed, which, with Reinecki's salt ($NH_4[Cr(NH_3)]_2(SCN)_4$), give typical branch-like crystals. With bromine in potassium bromide solution, aesculin gives typical black, star-like crystals; the sublimate darkens without crystal formation, probably owing to slight decomposition on sublimation. The reaction with bromine may also be used on sections of the tissue. *Rhinanthin* is present in the seeds of some grasses and cereals. When a section of tissue coating the glucoside is heated for ½ to 1 hour to 320° C., it gives a crystalline sublimate; when heated to 400° C., or higher, the sublimate consists of small drops of oil, containing some crystals and powder. The sublimate obtained at 320° C. does not saponify with saturated alcoholic potassium hydroxide solution, but that obtained at 400° C. is easily saponified, and then gives typical rosettes of crystals. The sublimate obtained at 320° C. gives characteristic crystals with bromine in potassium bromide solution; the same crystals are not easily distinguished when the test is carried out in the tissue, but are obtained from the alcoholic extract of the seeds or from the expressed sap.

The sublimate obtained at 420° C. gives characteristic crystals with bromine which may be distinguished among the distributed particles of the oil, or, if the saponified sublimate is used, among the products of saponification. *Syringin* is found in the bark and leaves of the lilac. When a section of the bark, or its concentrated alcoholic extract, is heated to about 360° C., the sublimate consists of needle-shaped crystals. When the aqueous extract, after removal of proteins with lead acetate, is treated with bromine in potassium bromide solution, the formation of crystals and of a dark precipitate is observed. Sections of bark tissue give the same crystals when treated with bromine in potassium bromide solution. *Saponarin* is found in the leaves of the common elder. The pure substance or leaves, or their pyridine extract, when sublimed in the usual way at reduced pressure at 360° C., give fine needles, similar to those from aesculin. The glucoside gives a yellow solution with alkalis and a blue colour with iodine in potassium iodide solution. *Digitonin*, from digitalis, can be sublimed at 360° C., giving fine needles. With bromine, crystals similar to those obtained with rhinanthin are formed. *Salicin*, from the bark of willow trees, sublimes at 360° C., giving fine needle-shaped crystals. J. W. B.

Micro-chemical Examination of Glucosides. L. Rosenthaler. (*Mikrochem., Pregl-Festschrift.*, 1929, 302–307.)—Tests on the glucosides are carried out, using a combination of physical (melting-point determination, refractive index) and chemical methods. When the test is applied to tissue or biological material it is always necessary to make a control test for comparison on a similar sample, but with the glucoside removed by a suitable solvent. The various methods are:—(1) *Hydrolysis*, followed by the identification of the aglucone by hydrolysis with enzymes, is the most generally suitable for biological material. Hydrolysis with acid is used when the aglucone is insoluble in water, that is, for salicin and saponin, digitalis and strophanthus glucosides. Micro-sublimation is used for arbutin, which decomposes, giving its aglucone, which can be identified in the sublimate. (2) *Colour Reactions* generally apply also to carbohydrates, which should not be present. Concentrated sulphuric acid tends to destroy tissue, and is better used diluted with water or alcohol. For colour reactions with alkalis, concentrated aqueous or alcoholic potassium or sodium hydroxide is used. For distribution tests on tissues gaseous ammonia may be used. Reactions with ferric chloride are not usually sufficiently sensitive, and the reagent is unsuitable for tests on the distribution of glucosides in tissues. Nitric acid should be diluted for use with tissues. (3) *Precipitation Reactions.*—The precipitation reagents for the glucosides of high molecular weight are: tannin, hydrobromic acid, silico-molybdic acid, and similar substances; these also precipitate proteins and alkaloids, which should not be present. Ammonium sulphate also precipitates glucosides from their aqueous solutions. Special precipitation reagents include metal salts and salts of alkaline earth metals for glucosides of acid properties, such as saponin, which is precipitated by lead acetate or baryta water; these reagents also precipitate salts of organic acids. In tissues which adsorb the heavy metals it is not always possible to confirm the formation of the salt of the glucoside, after washing out the reagent, by precipitating the heavy metal with hydrogen sulphide. Stearin is a precipitant

for digitonin and other glucosides similar to saponin. In tissues, the precipitation does not always occur in the original position of the glucoside, but usually at the border of the section. Nitroso-dimethylaniline is sometimes used for the phenyl-glucosides, such as arbutin, which gives a characteristic addition product. Chlorine or bromine derivatives which are slightly soluble, may be used to identify the glucoside or aglucone. For distribution tests in tissues the halogen should be used in gaseous form. (4) *Biological Reactions.*—An example is the solution of red blood corpuscles by haemolysing glucosides. No other haemolysing substance should be present. J. W. B.

Specific "Spot" Test for Mercurous Ion. N. A. Tananajin. (*Ukrainski chemitschni Shurnal,* 1930, **5**, 63–4; *Mikrochem.*, 1931, **9**, 95.)—A drop of saturated sodium nitrite solution is placed on a filter paper, and a small drop of the test solution is put in the middle, while the paper is still moist. A brown fleck indicates the presence of mercury. The test is specific for mercurous ions, the smallest amount recognisable being $0{\cdot}2\gamma$ of mercury in a dilution of 1 : 10,000. The presence of coloured cations, such as chromium, iron and cobalt, reduces the sensitiveness. J. W. B.

Use of Diphenylthiocarbazide for the Detection of Magnesium. P. Agostini. (*Annali Chim. appl.*, 1930, **20**, 235–238; *Mikrochem.*, 1931, **9**, 96.)—This "spot" test may be carried out on a "spot" plate, or on a filter paper impregnated with the reagent. When two drops of a cold, saturated alcoholic solution of diphenylthiocarbazide are added to a drop of the test solution, and then excess of ammonia is added, a red gelatinous precipitate, or a red coloration, is formed in the presence of magnesium. The reaction is specific for magnesium, which may be detected in a dilution of 1:300,000. The reagent,

$$S=C\begin{matrix}\diagup\ NH.NH.C_6H_5\\ \diagdown\ NH.NH.C_6H_5\end{matrix},$$

is formed by the action of carbon disulphide on phenylhydrazine. J. W. B.

Micro-Determination and Separation of Calcium and Magnesium. K. L. Maljaroff. (*Mikrochem.*, 1931, **9**, 132–135.)—The method is applicable to the determination of about 10 mgrms. of calcium and magnesium, when present as carbonate, oxide or hydroxide. The mixture must contain none, or not more than a trace, of the alkali carbonates. The method is designed for the analysis of natural and artificial carbonates and oxides, such as magnesite, dolomites and technical calcium and magnesium carbonates. The separation utilises the different solubilities of the oxides in water. *Method.*—The powdered sample is ignited in a platinum crucible for about 20 to 30 minutes, to drive off organic matter, to render the iron and aluminium insoluble, and to convert the calcium and magnesium into oxides. The crucible is cooled in a desiccator over soda-lime, and the contents are then transferred to a conical flask, about 60 to 80 c.c. of water (free from carbon dioxide) being used to dissolve all the calcium oxide. The mixture is rapidly heated to boiling, and filtered rapidly through a small, quick-filtering filter paper. The precipitate is washed by decantation with small amounts

of water. The filtrate is titrated with 0·05 to 0·2 *N* acid, methyl orange being used as indicator. The acid used is equivalent to the calcium oxide. The filter is added to the precipitate, and the magnesium oxide is dissolved in a small excess of 0·05 to 0·2 *N* acid, with slight heating, and the excess acid is titrated against sodium hydroxide solution, methyl orange being used as indicator. The acid used is equivalent to the magnesium oxide. When sulphuric acid is used for the titration the iron and aluminium oxides do not dissolve. Comparative analyses of dolomite and magnesite on the micro scale, and on the macro scale (calcium being weighed as oxalate and magnesium as phosphate), gave excellent agreement. Artificial mixtures of calcium and magnesium carbonate analysed gave differences between calculated and found percentages of less than $\pm 0{\cdot}3$ per cent. J. W. B.

"Spot" Test for Nitrites. F. L. Hahn. (*Mikrochem.*, 1931, **9**, 31–33.)—The diazo reaction is used as a "spot" test for identifying nitrites. The sensitiveness of the test has been increased by improving the preparation of the impregnated filter papers, so that the smallest amount recognisable is $2{\cdot}5-5{\cdot}0 \times 10^{-5}\gamma$ and the limit of dilution is 10^{-7}. The naphthylamine oxalate reagent is prepared by dissolving one part of oxalic acid in alcohol on the water-bath, and then adding one part of α-naphthylamine, dissolved in a little alcohol. After cooling, the crystals that separate are filtered off, washed with alcohol and ether, and dried in a vacuum over potassium hydroxide; they are kept protected from laboratory air, which always contains nitrous acid (from Bunsen burners). Before impregnating the filter paper it must be cleaned by steaming as follows:—The filter paper is hung from a platinum hook, inside a large test tube, supported from the stopper, and the tube is heated on a water-bath while a current of steam is passed through it for 5 minutes. A solution of 1 grm. of α-naphthylamine oxalate and 1 grm. of pure sulphanilic acid and 0·2 grm. of potassium oxalate in 100 c.c. of hot distilled water is sucked into the test tube containing the filter paper until the paper is covered, when the impregnating solution is removed by means of a delivery tube which reaches the lowest part of the test tube. The tube is still kept on the water-bath, and the filter paper is dried inside it in a stream of clean air that has been passed through soda-lime and sulphuric acid. The filter papers thus prepared are colourless before the test, and are coloured red by nitrite. J. W. B.

Physical Methods, Apparatus, etc.

Immersion Liquids for Refractive Index Determinations. A. Mayrhofer. (*Mikrochem.*, 1931, **9**, 52–71.)—Instead of a large number of immersion liquids of varying refractive powers, it is suggested that a small number of liquids should be used in mixtures of varying proportions. Mixtures of low refractive index, large range, stability on keeping, and comparative chemical inertia are:—Water and glycerin: range, 1·333–1·465; cineole and paraffin oil: range, 1·456–1·482; paraffin oil and α-mono-bromnaphthalene: range, 1·482–1·658. High refracting mixtures include:—Paraffin oil and bromoform: range, 1·482–1·597; bromoform and α-mono-bromnaphthalene: range, 1·597–1·658; and bromoform and iodide: range, 1·658–1·740. These were used chiefly for testing the standard

mixtures by dilution. The volumes of the different constituents of the mixtures were measured by means of micro-burettes. There was excellent agreement between the calculated refractive index of the mixtures from the volumes and refractive indices of the two constituents, and that found by measurement. Even after keeping for four years the mixtures remained almost unaltered.

J. W. B.

Quantitative Spectrographic Analysis. A. Schleicher and J. Clermont. (*Z. anal. Chem.*, 1931, **86**, 191–216, 271–288.)—The methods of quantitative spectrographic analysis, as applied to the examination of commercial metals, are discussed; the authors give preference to Gerlach and Schweitzer's "absolute" method over Hartley and de Gramont's, based on observation of the "ultimate" lines. The papers deal with the determination of tin in lead, and of titanium, silicon, and iron in technically pure aluminium. For details reference should be made to the original papers.

W. R. S.

Reviews

THE SOIL AND THE MICROBE. By SELMAN A. WAKSMAN and ROBERT L. STARKEY. Pp. 250. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1931. Price 17s. 6d.

The scope of this work is indicated in the sub-title, "An Introduction to the Study of the Microscopic Population of the Soil and its Rôle in Soil Processes and Plant Growth," and, in accordance with this, the authors employ the term "microbe" in its widest sense. The subject matter extends from filterable viruses to earthworms, though the treatment mainly deals with the bacteria, actinomyces and fungi, with some consideration of the protozoa. The general relations between the soil and the plant on the one hand, and the microbial population on the other, are considered in the first three chapters. Chapters IV to VII deal, respectively, with the decomposition of organic matter in the soil, the fixation of nitrogen and ammonification, nitrate formation and reduction, and the transformation of mineral substances. The associations between soil organisms and the higher plants occupy Chapter VIII, and the effects of soil treatment on the micro-population are treated in Chapter IX. The final chapter brings the matter of the earlier chapters into relationship.

Generally, the book is well written and readable. The text is illustrated by 85 figures and diagrams and 56 tables from authoritative sources; the value of the figures, however, would have been greatly increased had the authors indicated the magnifications. Though the sources of the illustrations are acknowledged, the very few names mentioned in the text appear to have been left in by oversight. Loose writing occurs occasionally; as an example, "Each plant seems to be quite capable . . . of transforming sunlight into available food . . ." (p. 181) may be quoted.

The treatment throughout is naturally, from the size and scope of the book, very generalised. It should appeal to the student of agriculture and to the general reader, for whom it appears to be intended. There is no bibliography, but at the end of each chapter there is a short list of text-books dealing with the subject considered.

F. E. DAY.

RECENT ADVANCES IN ORGANIC CHEMISTRY. By ALFRED W. STEWART, D.Sc. Vol. I. Pp. 428. Vol. II. Pp. 432. Sixth Edition, Revised and Enlarged. London: Longmans, Green & Co., Ltd. 1931. Price, 21s. net per vol.

This book, in its main outlines, is now fairly well known, seeing that a sixth edition has been called for. The present volumes follow on the lines of their predecessors, the text having swollen by some ninety pages, owing to the inclusion of some new information on large ring compounds, strainless carbon rings, di- and tri-terpenes and the stereochemistry of diphenyl compounds. Extensive revision has resulted in the chapters on carbohydrate constitutions and anthocyanins, containing an account of much recent work which has been done in these important and interesting branches of organic chemistry. Nevertheless, in spite of much revision and of the volumes bearing the date 1931, it may be questioned whether the work of the last ten years receives adequate attention.

Many readers of the Journal of the Chemical Society will be surprised to read that "Up to the present, the full implications of the Lewis atom have not been whole-heartedly applied in the field of organic chemistry, as the matter is a complex one; but, possibly, before long, something will be done in this line of thought" (Vol. I, p. 17). Their surprise will not be lessened when, on coming to the chapter on "Orienting Influences in the Benzene System," they fail to find the names of Debye and Ingold, or any reference to the work of Robinson later than 1922. In the opinion of the reviewer, the chapter on "Some Applications of Electronics to Organic Chemistry" is hesitant and out of date. The amplification of this section would, to a large extent, render unnecessary the chapter on "Structural Formulae and their Failings."

The concluding sentence of the chapter on Unsaturation runs: "It seems possible that, as the electronic ideas of G. N. Lewis become more generally applied to organic chemistry, we may gain some clearer views on the subject of unsaturated compounds; for his conceptions of firm and looser groupings of electrons seem peculiarly adapted to elucidate many of the problems which have been touched upon in the foregoing pages." Following a brief account of Sugden's work on the parachor is the sentence (Vol. II, p. 24): "It appears that a distinction must be drawn between two kinds of double bonds: the non-polar and the semi-polar." From a perusal of these extracts the average reader would scarcely get the impression that one of the admittedly outstanding achievements of the electronic theory of valency has been its prediction of two types of double bond, and that there are now available three experimental methods for the detection of the presence of the semi-polar bond.

The formula RN $\equiv$ C for *iso*-nitriles, given on p. 27 of Vol. I, has been abandoned for many years.

The chapter on "The Diphenyl Problem" is of a quasi-historical character, and, in addition to a certain looseness of phrasing—"On hydrolysis, this ester yielded a surprise" (p. 314), and a slight ambiguity of formulae (p. 319)—presents the facts in a less striking and less precise manner than has already been done in the Annual Reports of the Chemical Society (1926, 119; 1927, 100; 1928, 114).

Although Professor Stewart deplores the neglect of "the historical branch of organic chemistry" (Vol. I, p. 407), yet a consideration of the development of theoretical organic chemistry since the opening of the present century appears to bring him but little joy—"the subject has yielded very little beyond some minor ideas . . ."; newer subjects have been "drawing the more original minds away from organic problems. The formula of triphenylmethane is certainly a less entrancing subject than, say, the peculiar phenomenon of *iso*-sterism, and it is only natural that inquiring intellects should concentrate themselves by preference upon matters which seem more fundamental than problems of molecular structure" (Vol. I, p. 17). But one joyful note appears—"There is, however, no reason to despair of the future of organic chemistry." "What is urgently needed is a completely new line of development" (Vol. I, p. 17). Is it possible that the author is propounding this in his concluding chapter where reagents are classified as "general" or "specific," or subsequently, after a consideration of the behaviour of hydroxylamine as an oxidising agent, as "synthetical" or "analytical"? (Vol. I, p. 402).

Professor Stewart has collected much useful and interesting information on natural organic compounds, but any book dealing with "Recent Advances" must meet with severe competition while we have the Annual Reports of the Chemical Society as a standard for comparison.

Before the book passes into another edition the elimination of terms such as "parachoric values," "non-iogenic carbon derivatives," might be considered, as well as a loose sentence (Vol. I, p. 254), where it is implied that a synthetic body is both isomeric and identical with trigonelline.

A few misprints in either formulae or text have been noted:—Vol. I, pp. 249, 261, 309, 335; Vol. II, pp. 7, 141, 171.

J. KENYON.

RECENT ADVANCES IN PHYSICAL CHEMISTRY. By S. GLASSTONE, Ph.D., D.Sc. Pp. 470. London: J. A. Churchill. 1931. Price 15s.

There are two reasons why this book will appeal to many readers of THE ANALYST: one is that it is directed more particularly to "chemists who, having started on a professional career . . . find they have neither time nor opportunity to keep in touch with modern developments in physical chemistry" as well as to the student, and the other is that it sets out quite clearly what we do know and have learnt in the past decade, but in such a way as to bring prominently into relief what a lot there is we do not know. Physical chemistry is, perhaps, the most important branch of our science because it deals so much with the fundamentals, the nature and properties of the atom and of the molecule; what is valency, why and how do reactions take place, what is solution, and what does catalysis mean?

Dr. Glasstone deals with the atom briefly and clearly; we almost begin to

know about it, thanks to Rutherford, Bohr, Aston, Planck and others. The electronic theory of valency, similarly, illuminates a dark place, yet there are so many obscure phenomena here that the theory becomes elaborate—might one say over-elaborate—to meet some of them and others are not met at all. The parachor of Sugden dispels some of our darkness on the structure of compounds and molecules: the parachor is briefly explained as the molecular volume of a compound when its surface tension is unity—an additive property of fundamental import. This much is bright and not too difficult.

Soon after this we plunge into obscurity: the chapters on reactions and catalysis bring out how little we really know of how or why even the simplest reactions take place; the path is strewn with the remains of ingenious theories destroyed by obstinate facts, but there are bright oases (even landmarks) to describe, and real discoveries to chronicle. The theory of even bimolecular reactions is so complex, and in part so uncertain, that one wonders whether there be not yet some unifying principle undiscovered but underlying all reactions; calculations based on vibration, on numbers of collisions, on critical energy, heat of activation, and so on, seem, like the theories of the expanding universe, to be so elaborate as to lose touch with reality, as well as with simplicity.

The chapter on solubility is a welcome change from the complexities of reactions; the internal pressure theory does give practical help, and even guidance, towards the choice of solvents for experimental purposes. The modern dissociation theory, too, is well described (though it is rather mathematical), together with the support it has received from *X*-ray crystallography, so that even if electrolytic theory is not yet complete and free from anomalies, it is at least much more firmly grounded than it was fifteen years ago.

It is obviously impossible to enter here into details or to criticise matters included or omitted; it suffices to say that the book is well written, clear and not too mathematical. It will not be read without an effort by most chemists, but the result of that effort will be a clearer insight into the underlying principles of our science. We are indebted to the author for sifting and pre-digesting a vast amount of complex material and setting before us a well-balanced diet in which the growth-promoting factors are not lacking.

H. E. Cox.

DIZIONARIO DI MERCEOLOGIA E DI CHIMICA APPLICATA. Vol. III, NAFTALINA TO SENA. By Professor G. VITTORIO VILLAVECCHIA AND OTHERS. Fifth edition, revised and enlarged. Milan: Ulrico Hoepli. 1931. Price 60 lire.

The contents of this volume, which follows I and II (reviewed in THE ANALYST for May, 1930) after the lapse of about eighteen months, proceed along the same general lines as the former editions.

Owing to the wide scope of the subjects treated, the information given is necessarily somewhat concise in certain particulars, and in some instances, as in the short article on the thyroid gland under the heading "organotherapeutic agents," is not quite up-to-date. Of special interest are the references to adulterations and alterations to which products are subject, to steps taken to prevent fraud, etc., and the same may be said of the statistical data concerning production,

importation, and exportation. As a rule, the last year for which such data are quoted is 1928 or 1929.

As in volumes I and II, a number of new subjects are here considered, and the fact that sections dealing with oysters, sardines, and feathers are found will indicate how extensive a range is covered. The numerous other topics reviewed include naphthalene and its derivatives, nickel, nitrates, essential and other oils, gold, barley, oxygen and oxides, bread, wood pulp, edible pastes, medicinal lozenges and plants, potatoes, hides, pepper, per-salts, pearls, fish, petroleum, precious stones, pills, gunpowder and smokeless powders, metal-cleaning materials, tomatoes, porcelain, perfumery, rhubarb, radium, resins, rice, roses, sands, sago, salt, salicylates, blood, soaps, meerschaum, slags, rye, senna, etc.

Touching the arrangement of the subject matter, it would appear more rational to consider silver nitrate and mercury oxides under the respective headings silver and mercury, instead of giving them separate sections under the titles nitrate of silver and oxides of mercury. The alphabetical index, to appear when the work is completed, should facilitate its use as a dictionary.

As in the two earlier parts, in this, also, the English equivalents are mostly accurate, although a considerable number of obvious English and foreign misprints occur, *e.g.* heat's foot oil, touche stone, quebracko, naphtaline, etc., Geteshead, sintetic, essencs, and so on. "Lachgas" is given as an English name for nitrous oxide (the heading is here protossido di azoto), and "reactives" is found instead of "reagents."

The volume comprises 1044 columns, two on a page. The principal type is good and easily readable, but for statistical matter, etc., a rather small type is employed. Even with our depreciated currency, the price is commendably low.

T. H. POPE.

Publications Received

CHEMICAL EMBRYOLOGY. By J. NEEDHAM, M.A., Ph.D. 3 vols. Pp. 2021. Cambridge University Press. 1931. Price 105s. net.

SOIL CONDITIONS AND PLANT GROWTH. Sir E. J. RUSSELL, D.Sc., F.R.S. Sixth Edition. Pp. 636. London: Longmans, Green & Co. 1932. Price 21s. net.

EXAMINATION OF WATER. By W. P. MASON. Sixth Edition. Pp. 224. London: Chapman & Hall. 1931. Price 18s. net.

POTENTIOMETRIC TITRATIONS. By I. M. KOLTHOFF and N. H. FURMAN, Ph.D. Second Edition. Pp. 482. London: Chapman & Hall. 1931. Price 18s. net.

QUANTITATIVE ANALYTISCHE MIKROMETHODEN DER ORGANISCHEN CHEMIE. By C. WEYGAND. Pp. 279. Akademische Verlagges. M.B.H. Leipzig. 1931. Price M.18.