THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

A MEETING of this Section was held in Manchester on December 11th. The Chairman (Mr. A. R. Tankard) presided over an attendance of forty-three, which included Dr. E. B. Hughes, Treasurer of the Society.

The following papers were read and discussed:—"The Practical Treatment of Dairy Effluents," by C. A. Scarlett, B.Sc., A.K.C., F.I.C.; "Non-alcoholic Wine," by C. J. H. Stock, B.Sc., F.I.C.; "A Note on Solutions of Hydrogen Peroxide," by C. J. H. Stock, B.Sc., F.I.C.; "The Detection of Glucose Syrup in Jams and Honey," by G. D. Elsdon, D.Sc., F.I.C.; "Note on Nigerian Ginger," by G. D. Elsdon, D.Sc., F.I.C.

Obituary

JOHN AUGUSTUS VOELCKER

OUR veteran Past-President, who died on November 6th, in his eighty-fourth year, was the second of the five sons of the late Dr. Augustus Voelcker, F.R.S. He was born on June 24th, 1854, at Cirencester, where his father was Professor of Chemistry in the Royal Agricultural College, and some of his early school days were spent at a preparatory school in the not distant town of Berkeley. In 1864 his father—who had become Consulting Chemist to the Royal Agricultural Society in succession to the late Professor Way—resigned his Professorship and removed to London, where the education of his sons was continued at University College School. At the end of his school course, in which he began the study of chemistry under the late Temple Orme, John went on to University College, where he took successively (with Honours) the degrees of B.A. and B.Sc., his chemical teacher being the late Professor Williamson. During his studentship most of his vacations and other available "off-times" were spent in the laboratory of his father in Salisbury Square, Fleet Street, as were those of his brother, E. W. Voelcker, who was a student at the Royal School of Mines, and who will be remembered not only

as another of our late Past-Presidents, but also for the services which he rendered to the Society for many years as Treasurer. It happened that the writer of this notice was at that time a pupil of Dr. Augustus Voelcker, and so there began an early and lifelong friendship with both the brothers.

During Voelcker's years at University College he found an outlet for physical energy on the racing track, establishing a reputation as a long-distance runner, and becoming the first secretary of the College and Hospital Sports Club. His interest in athletics was maintained throughout his life, he having been an active member of the Committee of the London Athletic Club (of which he was twice President) and of the Thames Hare and Hounds, whose cross-country runs he rarely failed to attend. When the natural waning of muscular adaptability reduced his personal participation in the more strenuous forms of athletics to that of an interested spectator, he took up shooting and fishing as his outdoor recreations and, like his brother, became skilled with the "dry fly." This reference to the sporting side of his life is made here because the writer considers that it was not without its bearing on his character and life-work.

On leaving University College, Voelcker went to Giessen, where he took chemistry under Professor Naumann and agriculture under Professor Thaer, and obtained his doctor's degree for a dissertation dealing with the molecular composition of apatite and other forms of naturally occurring calcium phosphate. Later in life, on the occasion of the visit of the Royal Agricultural Society to Cambridge in 1894, he received from that University the Honorary Degree of M.A.

After his career at Giessen he returned to work with his father, by whom he and his brother were later taken into partnership under the title of Dr. Augustus Voelcker & Sons.

Some time before this the laboratory in Salisbury Square had been supplemented by a second laboratory built as an annexe at the rear of the premises of the Royal Agricultural Society in Hanover Square, and it was chiefly here that Voelcker worked until the death of his father in December, 1884, when he was appointed in succession to him as Consulting Chemist to the Society, an appointment which he still held up to the time of his death, covering a period of over fifty years.

During this long tenure of office he naturally came into personal association with most of the well-known leaders of agricultural thought and practice, and had opportunities of visiting farms in most parts of the country and of familiarising himself with diverse systems of husbandry and stock management. Of these opportunities he was keen to avail himself, and he had a characteristic habit of making meticulous notes of all that he observed, preserving them for reference in his advisory work, which brought him a constant flow of correspondence; and the advice that he was able to give soon came to be generally received with well-justified confidence.

In addition to the busy routine of analytical and advisory work for members of the Royal Agricultural Society, there devolved upon him, immediately on his appointment, the no light burden of the virtual direction and management of the Woburn Experimental Station at Crawley Mill Farm, which had been established in 1876 on the estate of the Duke of Bedford and carried on up to this time under

the superintendence of his father, in association with the Council's Chemical Committee.

The expenses of this station were defrayed by the Duke of Bedford up to the year 1910, when his financial support was discontinued in view of a grant of £500 per annum made by the then newly established Development Commission. All further expenditure on the farm and station was undertaken by the Society up to the year 1921, when its Council unfortunately decided to abandon the work. Hereupon Voelcker, loth to contemplate the "scrapping" of Woburn and all that it stood for, courageously obtained from the Duke of Bedford the transference of the lease of the farm to himself, and with monetarily self-sacrificing devotion and with only the aid of the grant of the Development Commission, carried it on at his own risk for five years until, in 1926, it was taken over by the Lawes Agricultural Trust. Voelcker, however, remained Honorary Director of the station until 1936.

The establishment of the Woburn Station was originally for the purpose of practically testing the comparative residual manurial value of high nitrogenous and low nitrogenous feeding stuffs from the point of view of compensation to outgoing tenants for foods consumed on the farm, in view of the conclusions derived from the earlier work of Lawes and Gilbert; and, incidentally, for the repetition, on a very different type of soil, of the experiments on the continuous growth of grain crops which had long been carried out by Lawes and Gilbert at Rothamsted; but much other experimental field work had been added from time to time. A further important addition to the Woburn investigations was made in 1897 by the bequest to the Royal Agricultural Society of £10,000 by the late Mr. E. H. Hills, for the purpose of experiments on the influence on plants and soils of what were then regarded as less commonly occurring chemical elements. This led to the establishment of a local laboratory and pot-culture station. Investigations under this bequest were carried on by Voelcker for twenty-three years with the local assistance at first of Dr. H. H. Mann, and later, successively, of H. M. Freear, J. Crabtree and A. Blenkinsop, until 1921, when the Society, on relinquishing its connection with Woburn, made over the Hills Bequest to the University of Cambridge. Up to this time the multifarious Woburn researches, both in the field and in the pot-culture station, were recorded yearly in the long series of reports by Voelcker printed in the volumes of the *Journal of the Royal Agricultural Society*, and were, perhaps, not very much known outside of the circle of readers of that journal. The side of the work constituting the field experiments has, however, been lately focussed (in 1936) in the volume of *Fifty Years of Field Experiments at the Woburn Experimental Station*, by Sir John Russell and Dr. Voelcker (see review, ANALYST, 1937, **62**, 237).

As regards the primary original object of the field experiments the results have been of momentous and, at the same time, disappointing, interest, inasmuch as that they have persistently indicated that, at any rate, on the type of land exemplified by the light Woburn soil, the superiority of the residual manurial effect of feeding stuffs rich in nitrogen as compared with those of the less nitrogenous and more farinaceous foods has not been in accord with long-established assumption. Apart from the Woburn results, investigation at Rothamsted and

elsewhere on the composition of farmyard manure, as affected by the foodstuffs consumed in making it and by the chemical changes incidental to its storage, had been leading to the conclusion that the original tables of Lawes and Gilbert, bearing upon the question of compensation to outgoing tenants for the unexhausted value of their contributions to the soil, called for revision. This revision was undertaken by Voelcker and Sir A. D. Hall, whose modified compensation tables were published in a joint paper in the journal of the Royal Agricultural Society of England for 1902. A further paper on the subject by Voelcker and Hall appeared later in the Journal of the Royal Agricultural Society of England for 1913, in which still further modifications were made of their earlier tables, and this later version, with revision from time to time by Voelcker, in view of fluctuations in the market value of nitrogenous phosphatic and potassic fertilisers, is still generally accepted in England for compensation valuations by the Central Association of Tenant-Right Valuers; but the practical experience on the Woburn Farm has done much to emphasise the danger of their too literal application without regard to variations of soil and local conditions.

One of the most spectacular results in Voelcker's field work on the Woburn Farm was the demonstration that the long-continued use of sulphate of ammonia on soil deficient in lime may result in the almost complete suspension of fertility owing to the leaching out of the original lime of the soil in the form of soluble calcium sulphate; with, however, the further consolatory experience that fertility could be completely and promptly restored by a dressing of lime, thus indicating the simple means by which the otherwise beneficent effects of sulphate of ammonia can be enjoyed on land naturally poor in lime without fear of deterioration.

The recent book of Russell and Voelcker contains no record—beyond a mere passing reference—of the special pot-culture work carried out under the Hills Bequest, but a brief summarised account of it was contributed by Voelcker himself to the Journal of the Royal Agricultural Society of England for 1923. The special elements or substances of which the effects were tested included manganese, lithium, barium, caesium, cerium, strontium, lead, zinc, tin, chromium, copper, boron, arsenic, iodine, bromine, fluorine, and "radio-active" ores.

An important temporary diversion of Voelcker's activity occurred in 1889, when, at the request of the Indian Government, the Secretary of State for India decided to send out from England an agricultural chemist to make a tour of enquiry in India and to advise upon the course to be pursued for possible improvements in Indian agriculture. For this duty, on the recommendation of the late Sir James Caird, Voelcker was chosen and, with the permission of the Royal Agricultural Society, he visited India and spent a full year there making two extensive tours of the Empire. The result was a report of some 450 pages on "The Improvement of Indian Agriculture" (Eyre & Spottiswode, 1894). This report had a far-reaching effect on the subsequent development of Indian agricultural education and of the pursuit there of agricultural chemistry, largely encouraged by the work carried on for many years in India by Voelcker's former assistant, the late Dr. Leather, who was sent out as an immediate consequence of Voelcker's report. Although that report was received at the time with much congratulatory approbation, the conferment on its author of the distinction of

C.I.E. was delayed until as recently as 1928; it was given then presumably as a consequence of a new enquiry instituted under the auspices of Lord Linlithgow, when attention was re-directed to the report of 1894.

As regards Voelcker's long connection with our own Society, it may be recorded that he joined us in 1886, became a Member of Council in 1888 and our President in 1901 and 1902, and remained on the Council in the capacity of Past-President until the time of his death. He was constant in attendance, both at our general meetings and at the Council table and at various committee meetings at which his knowledge and experience were a valuable asset. Although he contributed often to our discussions, his contributions to THE ANALYST in the form of papers were but few. They included notes on "Water from Wells near Churchyards" (1894); "Cottonseed Cake (distinction between Egyptian and Bombay)" (1903); "Hairballs in Sheep" (found to consist of aggregates of the hairs of Crimson Clover) (1903); "Effects of Borax on Vegetation" (Roberts, Smetham and Voelcker) (1918); and "Woody Fibre in Feeding Stuffs" (J. A. and E. W. Voelcker) (1918).

He was a Member of the Council of the Chemical Society in 1891–95 and 1902–4; he also served many periods on the Council of the Institute of Chemistry and was one of its Vice-Presidents from 1896 to 1899. For many years, and up to the time of his death, he was a member of the Committee of the London Farmers' Club, of which, in 1908, he was elected Chairman, a distinction which he especially valued in view of his father having occupied the same position thirty-three years earlier. He was also a member of the Advisory Committee appointed to assist the Ministry of Agriculture under the Fertilisers and Feeding Stuffs Act of 1926.

He was consulting chemist to the Royal Horticultural Society, as well as to the Royal Agricultural Society, and also to the Bath and West of England Society; and he acted as Official Agricultural Analyst for Buckinghamshire, Oxfordshire, Middlesex, Northamptonshire, Northumberland, the East Riding of Yorks, the Isle of Ely, and the County Borough of Oxford. Under the Food and Drugs (Adulteration) Act he was (jointly with his nephew, Mr. Eric Voelcker) Public Analyst for the Counties of Northampton, Buckingham and Oxford, and for the Borough of Banbury.

This notice would be incomplete without reference to yet another side of his activity which the writer feels that he would not have liked to be left unrecorded. When his father came over from Germany he settled first in Edinburgh, and there became a devoted adherent of the Presbyterian Church. His religious enthusiasm was passed on to his son, who was an active member of the congregation of St. John's Presbyterian Church, Kensington, which he attended regularly from 1870 onwards. He became a deacon in 1884, and an elder in 1897, acting for the last twenty-four years as Sessions Clerk; and he did much outside work in connection with church extension in the community to which he belonged. Strong, however, as was his own religious conviction, this was unmarred by sectarian prejudice or by lack of tolerance for views which differed in religious or philosophical complexion from his own.

In personal and professional matters his attitude was always dominated by a strict sense of truth and straightforwardness, and there were sometimes occasions

when, in matters of scientific interpretation or of administrative policy, he found it not easy to yield to argument based on views which happened not to be consonant with those to which he had felt himself conscientiously impelled. But any differences which thus arose were seldom allowed to interfere with personal friendship, and his essential amiability of character was aided by the possession of a happy endowment of that sense which sometimes throws oil on troubled waters —the sense of humour. The knowledge acquired during his long and wide experience was always ungrudgingly placed at the disposal of any colleague who sought his advice or assistance; and his genial presence and handsome figure—bowed a little in his declining years—as well as his loyal friendship will be affectionately remembered by very many and—if yet another personal allusion may be forgiven—by none more than by the writer.

He married, in 1884, Alice, eldest daughter of the late Mr. W. Westgarth, formerly of Melbourne, and leaves one son and two daughters. His eldest son died in early infancy, and his second son lost his life in the war.

His partner, Mr. Eric Voelcker, who succeeds to his practice and shared many of his official appointments, is the son of the late E. W. Voelcker, his brother.

BERNARD DYER

The Contamination of Whale Oil with Fuel Oil

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

(*Read at the Meeting, December* 1, 1937)

PART I

THE great advances of recent years in the production of whale oil in floating factories, and the use of fuel oil for providing the motive power of ships, have introduced many interesting problems.

By no means the least important and difficult of these is that the same tanks are commonly used for carrying fuel oil to the factory ships on the outward journey of a transport ship and for bringing whale oil home in bulk.

Great precautions are taken to clean the tanks efficiently between cargoes; these include steaming for long periods, scraping, and applying a coating of silicate "paint" to the whole of the interior surfaces. Occasionally, however, the whale oil becomes contaminated with fuel oil, either through faulty cleaning or by leakage from adjacent tanks at rivets or the edges of plates.

As little as 0·01 per cent. of fuel oil seriously damages the colour of whale oil. Practically all whale oil is hydrogenated before use, and many authorities hold that these traces of fuel oil seriously retard hydrogenation, increase its cost, and cause the hardened product to be of inferior colour and value. In considering the extent of the damage, the fact that fuel oils contain up to 3 per cent. of sulphur—a notorious catalyst poison—must be taken into account. Substantial claims

have been made from time to time for an allowance from the contract price of cargoes where fuel oil contamination has been suspected, and the commercial significance of the problem will be realised when it is mentioned that allowances up to 30 shillings per ton on several thousand tons of whale oil have been made at arbitrations dealing with these claims.

It became necessary in 1931 for us to review the existing suggestions for detecting traces of mineral oil in fatty oils and to devise a method for detecting and determining these minute traces of fuel oil.

As far as existing methods were concerned, the only one we could find which really approached the problem was one recommended by Lewkowitsch (*Chem. Rev. Fett- u. Harz.-Ind.*, 1907, **14**, 51; Abst., ANALYST, 1907, **22**, 122). He was concerned in following the work of Polenske in connection with the detection of small quantities of paraffin wax in lard; but his method appeared to be successful only when the quantities were of the order of 10 per cent. of the unsaponifiable matter. Briefly, his procedure was to boil the unsaponifiable matter with 2 to 3 ml. of acetic anhydride, under which conditions the paraffin wax was left unacted upon in the form of a drop.

In our hands this method proved quite successful for recognising quantities of the order of 0·05 to 0·1 per cent. of fuel oil in whale oil, but broke down entirely in the determination of quantities ranging from 0·005 to 0·02 per cent.

We modified this method, applying the more modern precautions in the saponification and extraction stages until we had developed a method which certainly gave us a measure of the hydrocarbons present in the oil.

Our next concern was that certain fish oils had been shown to contain natural hydrocarbons, and it remained to prove whether we had succeeded in effecting a separation of these from the hydrocarbons derived from fuel oil. Eventually we found that for all practical purposes the hydrocarbons of fuel oil were insoluble in acetic anhydride, whereas all the hydrocarbons natural to fish oil were soluble in that medium.

The most important advance in this procedure, however, was our discovery that it was necessary to cool a very highly diluted acetic anhydride extract for 24 hours in order to secure the necessary delicacy of separation of the small quantities with which we were concerned, and we must especially emphasise the point that proper separation cannot be achieved if it be attempted immediately upon cooling the acetic anhydride extract.

Our method is somewhat lengthy and is admittedly empirical in parts. Its technique therefore calls for rather delicate manipulation and careful observation of details.

DESCRIPTION OF METHOD.—Twenty-four g. of sodium hydroxide* of analytical quality are dissolved in 20 to 25 ml. of water in a 1-litre flask, and 300 ml. of purified industrial methylated spirit* are added. The solution is warmed. One hundred g. of the oil to be tested are poured in, and the flask is shaken and warmed until the oil saponifies and the solution becomes homogeneous. An air-condenser is fitted to the flask, and the latter is heated on a hot plate for 2 hours with occasional shaking, the contents being kept gently boiling. The flask and its

* See Notes on p. 88.

contents are then cooled somewhat, and 370 ml. of distilled water are added. The fuel oil and the bulk of the unsaponifiable matter are now extracted with petroleum spirit.

It may be noted that certain of the constituents of the unsaponifiable matter of marine animal oils are not readily extracted from soap solutions by this solvent, while the unsaponifiable fraction of fuel oils appears to be extracted with ease. Petroleum spirit therefore effects a partial separation of some of the natural unsaponifiable matter from the fuel oil, and on this account is used purposely in our method.

The soap solution is transferred to a large separator and shaken violently while still warm with 300 ml. of petroleum spirit (b.p. 40° to 60° C.).* The liquids are then allowed to stand until they have completely separated.

The petroleum layer is removed to a 2-litre separating funnel containing 100 ml. of water.

Extraction of the soap solution is repeated four times more with 250-ml. quantities of petroleum spirit, the soap solution being kept warm throughout. If it is allowed to cool too much, separation becomes difficult and emulsions will form, but if warm, separation is rapid and complete.

The extracts are combined in the large separating funnel.

The next step consists in the removal of the bulk of the soap with which the extracts are contaminated.

The water is drawn off from the funnel, and the combined extracts are shaken with 50 to 80 ml. of a solution made by dissolving 40 g. of sodium hydroxide in 600 ml. of water and adding 400 ml. of alcohol (95 per cent.). The funnel is allowed to stand until the liquids separate completely and then the aqueous layer is run off.

Fifty to 80 ml. of a mixture of 30 volumes of alcohol (95 per cent.) and 70 volumes of water are run into the funnel, which is again shaken and allowed to stand until separation is complete, and the aqueous liquid is run off.

Washing is repeated alternately with the aqueous alcoholic alkali and the aqueous alcohol until three washes with each have been made. The petroleum solution is then washed twice more with the aqueous alcohol. It is then filtered through paper and the petroleum spirit is distilled off on a water-bath.

Weak alcoholic solutions are more efficient in removing soap from petroleum spirit than are aqueous ones. The solutions described are not strong enough to cause the removal of any unsaponifiable substances.

A second saponification and extraction of the unsaponifiable substances are now carried out in order to ensure the complete freedom of the extract from unsaponified oil and soap.

Twenty-five ml. of $N/2$ alcoholic potassium hydroxide are added to the extract, and the containing flask is attached to a reflux condenser and heated in a boiling water-bath for half an hour.

The solution is treated by the full extraction and washing processes laid down in the Society's Method for the Determination of Unsaponifiable Matter (ANALYST, 1933, **58**, 203), whereby all the unsaponifiable matter in the extract is

* See Notes on p. 88.

recovered. The solution is diluted with 50 ml. of water and extracted while just warm three times with 50 ml. of ether*; the combined extracts are washed with water twice, then alternately with $N/2$ aqueous potassium hydroxide solution and water (three times with each), and finally three or more times with water.

The ethereal extracts are then transferred to a 150-ml. carbon dioxide flask and the ether is distilled off.

The residue consists of a mixture of unsaponifiable matter natural to whale oil and the unsaponifiable fraction of the fuel oil. It usually weighs from 0·5 to 1 g.

Twenty-five ml. of acetic anhydride are added, and the flask is covered with a watch-glass and heated nearly to boiling for half an hour on a hot plate. Most of the material goes into solution. The flask is then cooled and allowed to stand for 24 hours at room temperature. If fuel oil is present it separates in the form of brown, oily, sticky droplets, even if only 0·003 g. (and sometimes less) is present.

Very rarely, slight crystallisation of sterol acetates takes place—usually in the body of the liquid away from the drops. In such cases a further 10 ml. of acetic anhydride are added and the heating and standing are repeated, when it is found that no sterol acetates crystallise.

The acetic anhydride is gently transferred to a small separating funnel, and any droplets which go with it are allowed to rise to the surface or stick to the sides.

The acetic anhydride is carefully run off on to a small filter-paper which catches any entrained droplets as the anhydride filters.

The carbon dioxide flask is rinsed with 10 to 15 ml. of fresh acetic anhydride, which is then poured into the funnel and swirled round. The droplets are allowed to rise as before, and the acetic anhydride is drawn off and used to wash the filter-paper. The washing is repeated twice more with 10 to 15-ml. quantities of acetic anhydride. All matter soluble in acetic anhydride is thus removed from the carbon dioxide flask, funnel and filter.

Such soluble matter includes sterol products, fatty alcohols and hydrocarbons natural to whale oil.

The carbon dioxide flask and the filter are washed with petroleum spirit, and the washings are added to the separating funnel until the latter contains 50 to 80 ml. of petroleum spirit.

The fuel oil residue dissolves in the solvent, and the solution is washed twice with $N/2$ aqueous alkali and three times with water to remove the last traces of acetic anhydride. It is then transferred to a weighed 150-ml. carbon dioxide flask. The petroleum spirit is distilled off on a water-bath, and the flask is heated for 5 minutes in a water-oven, allowed to cool and weighed.

The final weighings of the carbon dioxide flask must both be made with great care under identical conditions of temperature and humidity, and only after the flask has attained equilibrium with the surrounding atmosphere.

The appearance, consistence and colour of the extract are noted, and its iodine value determined by the pyridine-sulphate-bromide method, using the technique described by us (ANALYST, 1930, **55**, 5). By this method a considerable degree of accuracy is obtained, even if only as little as 5 mg. of material are available.

* See Notes on p. 88.

NOTES: (1).—Sodium hydroxide is often supplied in bottles sealed with paraffin wax. Care is necessary to ensure that no trace of this is allowed to fall into the bottle or to contaminate the alkali.

(2).—Industrial methylated spirit must be purified before use. A suitable method consists in refluxing 1 litre with 20 g. of vegetable oil (such as soya-bean oil or arachis oil) and 20 g. of solid sodium hydroxide for two hours and then distilling.

(3).—The petroleum spirit must be redistilled before use to ensure freedom from high mineral oil fractions or other contaminants.

(4).—It is preferable to redistil the ether before use, adding solid sodium hydroxide to the flask from which it is distilled.

A consideration of the method will show that the following precautions are taken:

(1) Double saponification ensures the complete saponification of the oil and that no glyceride remains. This is important, since glycerides of fatty acids are not in general completely soluble in cold acetic anhydride.

(2) Double separation of unsaponifiable matter ensures the removal of all soap. The only contaminants remaining are traces of free fatty acid and/or acid soaps, which are soluble in acetic anhydride.

(3) The volume of acetic anhydride used ensures complete solution of sterols, sterol acetates and acetylated products of other alcohols.

It will be clear that the method produces a product free from unchanged glycerides, soaps, sterols, alcohols and glycerol: the product can therefore contain hydrocarbons only.

It has been urged that, this being so, it remains to prove that any hydrocarbon separated is mineral in origin and not natural to the whale. We consider the evidence to be quite clear in this direction. It is as follows:

(1) No residue over 0·003 per cent. is ever recovered from a whale oil known to be uncontaminated—*i.e.* made in and transported by coal-burning ships.

(2) The characteristics of the residue—*i.e.* its colour, fluorescence, behaviour to solvents and iodine value—agree with those obtained from artificial mixtures of fuel oil and whale oil.

(3) We know of and have encountered no unsaturated hydrocarbons insoluble in acetic anhydride other than certain constituents of fuel oil. In making this statement we may mention that we have ourselves examined a large number of the more readily accessible unsaturated hydrocarbons. The point is dealt with only to a very limited extent in the literature.

Hydrocarbons are stated to occur naturally in whale oil, particularly in oils prepared from the body of the animals or from the organs, to the extent of some tenths of one per cent.

Professor J. C. Drummond has been kind enough to show us actual specimens of such natural hydrocarbons which he has himself isolated and which no doubt he will describe elsewhere. As a final proof that such hydrocarbons do not appear in our residue we have prepared them ourselves from 100 g. of whale oil by

following his technique (privately communicated), and have treated the product with acetic anhydride as described above. Under these conditions we found the hydrocarbons to be soluble and to leave no residue of droplets. Further, the addition, to the hydrocarbons so prepared, of the residue obtained from 0·015 g. of fuel oil, previously treated with alcoholic alkali and extracted from the latter under the general conditions of our method, led to a final brown residue of 0·009 g. of dark brown matter similar in character to that derived from fuel oil alone.

Hence, it is clear that the hydrocarbons naturally present in a normal whale oil do not interfere with, or add to the proportion of residue yielded by, the test.

RESULTS OF THE TEST.—When the test is operated upon either fuel oil or whale oil contaminated with known amounts of fuel oil, it is found that the final residue amounts to 50 to 90 per cent. of the fuel oil present. The actual proportion recovered depends partly on the nature of the fuel oil used and, to a lesser extent, on the proportion in the mixture. If there is 0·015 per cent. present, between 50 and 70 per cent. will be recovered in the majority of cases. It will be realised that this residue contains only a relatively small proportion of the asphaltes of the fuel oil, as these are only slightly soluble in petroleum spirit.

The residue from fuel oils and contaminated whale oils usually has an iodine value about 10 units higher than the original fuel oil, probably owing to the separation of the asphaltes.

The residue from pure whale oil, even if of No. 2 quality, does not exceed 0·003 per cent., and is usually below 0·001 per cent.

PART II

The recent development of the so-called "chromatographic" method of analysis of fatty residues—whereby certain constituents of solutions of unsaponifiable matter are adsorbed at different levels in a column of aluminium oxide—suggested to us a new method for detecting the presence of traces of fuel oil in whale oil and obtaining confirmation of the results of the method described in Part I of this paper.

Fuel oils are characterised by the presence of 10 per cent. or more of asphaltic or pitch-like bodies. We have found that when these oils are dissolved in petroleum spirit and the solution is passed through a column of activated aluminium oxide, all the asphalte is removed and remains at the top of the column. Further, if even minute traces of fuel oil are present in whale oil the asphalte is still removed under similar treatment and yields a characteristic and almost black layer whose size and intensity form a very good guide to the proportion of fuel oil present.

Uncontaminated whale oil often leaves an orange or light brown deposit which is unlikely to be mistaken for fuel oil; but we find that any doubt can readily be removed by extraction of the deposit with ether (in which the asphaltes dissolve) followed by re-adsorption of the extract after removal of the ether and solution in petroleum spirit.

If the adsorbed layer is now dissolved in ether the extract is pale yellow if the whale oil was uncontaminated, and dark brown if fuel oil was present in any proportion over 0·005 per cent. Even No. 2 and No. 3 whale oils, if uncontaminated, yield only a pale yellow extract.

The details of the method we have used are as follows:

DESCRIPTION OF METHOD.—A glass tube, 12 to 16 inches long and $\frac{2}{3}$ in. to 1 in. in internal diameter, is drawn out at one end and joined to a short length of glass tube of about $\frac{1}{4}$ in. diameter. The tube is fixed vertically, with its narrow end downward, through a cork into a filter-flask, and the lower end is plugged with cottonwool.

A suspension of activated aluminium oxide in petroleum spirit (b.p. 40° to 60° C.) is poured carefully into the tube and allowed to distribute itself evenly, gentle suction being applied meanwhile to the flask. The aluminium oxide column should itself, after packing, have a height of 6 to 8 inches, and a layer of petroleum spirit, 2 in. deep, is maintained over the top of the oxide until the test is made.

Twenty g. of the whale oil, previously filtered through paper at a temperature just sufficiently high to dissolve all stearine, are dissolved in 80 ml. of the petroleum spirit, and the solution is poured gradually through the tube, care being taken not to disturb the surface of the oxide. Filtration is assisted by gentle suction, and the upper surface of the liquid in the tube is kept well above the oxide surface.

When all the oil solution has been transferred to the tube and the liquid surface is about 2 inches from the oxide, the tube and column are washed by repeatedly filling with petroleum spirit and allowing filtration to proceed until the liquid surface is again 2 inches from the oxide. About 500 ml. of spirit should be used for the washing; at its conclusion the liquid is sucked as completely as possible from the tube and the appearance of the adsorbed layer is observed.

The contents of the tube are pushed out from the bottom by means of a glass rod, and the first inch or so of the column is shaken with about 50 ml. of ether. The ethereal solution is filtered, the filter is washed, the filtrate and washings are evaporated, and the residue is dissolved in 50 ml. of the petroleum spirit.

This solution is treated in a second column of aluminium oxide in exactly the same way as before, when traces of fuel oil—if present—leave a characteristic dark brown or black deposit, while uncontaminated whale oil gives either no visible deposit or a pale yellow stain.

The aluminium oxide column is washed with petroleum spirit as before and, after draining, is pushed out from the bottom. The top layers are extracted with ether, and the extract is evaporated.

The residue is dark brown if more than 0·005 per cent. of fuel oil is present in the whale oil, and pale yellow if the oil is uncontaminated.

6, MILNER STREET, S.W.3

DISCUSSION

Dr. E. F. ARMSTRONG remarked that he supposed that he was the first person to whom Messrs. Bolton and Williams had disclosed their method in full detail. He had had it demonstrated before him several times and had grown to know it intimately. Great dexterity had been used in working it out, every possible precaution had been observed from first to last so as to exclude anything which might interfere, and he could confirm how accurate it was. He was quite sure, having seen these tests and having himself made up some of the samples tested, that it was easy for an experienced operator to be certain to 0·005 per cent.

Professor J. C. DRUMMOND congratulated the authors on introducing valuable improvements in the technique for detecting the contamination of whale oil

with fuel oil, but he was not quite happy about all that they had said. When the unsaponifiable fraction of uncontaminated whale oil was submitted to adsorption technique it was sometimes found that it was not a question of 0·01 per cent. of natural hydrocarbons, but of very nearly 0·1 per cent. Apparently the hydrocarbon content of whale oil depended to some extent on the proportion of blubber-meat and liver-oils. The iodine value of such hydrocarbons varied from 90 to 160—a rather wide variation. Another point on which he was not entirely satisfied was the solubility of the natural hydrocarbons in acetic anhydride. It was difficult to believe that this solvent achieved a complete differentiation between these hydrocarbons and those of fuel oil. Had the authors of the paper carried out any tests on pure fuel oil? He himself had found that as much as 10 to 40 per cent. of the latter was soluble in acetic anhydride under the conditions of the Bolton–Williams test. The fluorescence of hydrocarbons from meat oil depended on the conditions of the cooking of the meat and bone oil. The direct adsorption test on the oil itself was very interesting and appeared to be a useful new method provided that one could be certain, by an appropriate test, that the dark colour at the top of the column was due to asphalt. Whale oils of poor quantity or containing minimum quantities of meat residue caused darkening of upper layers of the aluminium oxide, and it would be interesting to know how this differed from discoloration due to traces of asphalt. Had the authors made an elementary analysis of the hydrocarbons they had isolated, because he wanted to be quite certain that those hydrocarbons really represented material derived from fuel oil, and not a mixture containing in addition substances natural to the whale oil. The unsaturated natural hydrocarbons of whale oil certainly dissolved more readily in acetic anhydride. There was one point which had always worried him in dealing with this question of contamination of whale oil by fuel oil. The analytical results suggested that contaminations of 0·005 to 0·05 per cent. might occur in a consignment of 1000 tons. Instances where several hundredweights of fuel oil had escaped must be an extremely rare occurrence in oil-carrying vessels of modern design, where the fuel oil pipes were isolated from those used for conveying whale oil and where the cleaning of the tanks was very strictly supervised.

Mr. CYRIL MILLER said what interested him most as a lawyer was the question of damages. They were told how much contamination there was by fuel oil, and the tribunal had to come to some decision as to value. It was stated that there was 0·005 per cent. of fuel oil in the parcel. What was the damage? On the one hand, the buyer said: "If I pass this whale oil through my hydrogenation plant, I am going to be put to immense expense, and when I have got it out at the other end it is not going to look very nice." On the other hand, the seller said: "If there is a contamination of only 0·005 per cent., by the time the whale oil appears before the public in the form of margarine, they will know nothing about it." It was very difficult to say what the damage was. He was not satisfied that that was really the commercial point of view. Mr. Bolton had succeeded in convincing him that there was a serious amount of damage, but it was exceedingly difficult in such cases to assess that damage in terms of money.

Dr. E. F. ARMSTRONG remarked that Mr. Miller was quite right—and these things were not only costly. If a whale oil was sold as high-class No. 1 Grade Whale Oil and was contaminated with fuel oil, the recipient was bound to be suspicious almost immediately. Laboratory tests would show that the colour could not be removed by the ordinary methods of removing the fatty acids, etc., so that in the laboratory one was immediately conscious of the fact that the sample was not worth as much as ordinary whale oil. There the responsibility of the works chemist ceased and the responsibility of the manager or director began. The manager had a consignment of, say, 2000 tons of whale oil which he knew was contaminated, and he had to decide whether to put it through his plant in the ordinary way, knowing that after treatment it might not be fit for use in margarine,

etc. Such responsibility was too great for any reputable firm to take; accordingly the purchase would have to be treated as of inferior grade.

Mr. A. F. BEARPARK said that he had been merely the arbitrator in this case, he had not expected to take part in the discussion. He had listened with great interest to the remarks of Mr. Bolton, and also to what Mr. Miller, with his legal mind, had said, and he thought that he should still have come to the same decision as he had done previously, though he would not tell the meeting what that was. He very much appreciated Professor Drummond's point of view, and he thought that to a very great extent, if he might express the opinion, he was on the right lines. But he had said that from a commercial point of view the main question was one of colour. He ventured to differ, because the colour of whale oils prepared from the meat of whales might be bad, but that colour was easily removed by a commercial process, whereas colour arising from contamination with fuel oil was not removed by any commercial process. Having listened to what had been said, he was still unconvinced as to the possibility of detecting that very small percentage of fuel oil in whale oil. He, as a practical whaler, knew when whale oil was contaminated with fuel oil, but whether it was possible to swear to it he must leave to specialists such as Mr. Bolton and Professor Drummond.

Mr. A. L. BACHARACH suggested that it might be possible to discriminate between those coloured bands at the head of the absorption column that were due to chromogenic material natural to whale oil and those that were due to contaminating fuel oil. The former might possibly contain nitrogenous compounds, while the latter would certainly not do so. He called attention to the fact that this paper was the first in which the Society had been treated to an application of chromatographic methods. Paradoxically enough, the chromatograph was originally developed for analytical procedure and was only now beginning to be used by analysts.

Dr. J. GRANT wondered whether the authors had observed these colours under the ultra-violet light.

Mr. H. E. MONK remarked that the authors of this paper had been interested mainly in whale oil; the fuel oil had been incidental. His own interest was in the fuel oil. He had had to deal with waters that had been stated to be contaminated with fuel oil. He had found that the tests recorded were largely negative ones; had the authors any positive tests for fuel oil?

Mr. E. R. BOLTON, replying, said that Prof. Drummond had suggested a balance of errors, and this point had been thoroughly investigated, showing that the errors tended to underestimate the fuel oil; after all, they did actually separate and weigh fuel oil. He agreed that the hydrocarbons from fish oil exhibited a certain fluorescence, and thought that Dr. Grant had put his finger on the point in suggesting the use of ultra-violet light, which the authors had not tried. In reply to Mr. Monk's point as to the detection of fuel oil in water, he drew attention to the fact that the process of separation described was not just a single, simple test for fuel oil, but a series of operations to separate it from fish oil, and was not applicable to water. Mr. Bolton said that he would like to leave the other points to be dealt with by Mr. Williams.

Mr. K. A. WILLIAMS, replying, said that the authors had been engaged in cases involving these tests since 1931, and the last case had occupied about 10 months. He thought that most of the oil chemists in Europe had been concerned in one or other of these cases, and the meeting would realise that the tests had been subjected to the most searching criticism. Very many points had been raised at one time or another and had been settled satisfactorily after prolonged argument. He did not consider it possible to deal with all these points in a few minutes. The real answer to Professor Drummond, however, was that one never obtained any appreciable extract from whale oil known to be uncontaminated, even if the oil

were badly off-colour; whilst all the notable extracts were similar in characteristics to those yielded by artificially contaminated oils and by fuel oil itself. So far as the adsorption test was concerned, the authors had not yet investigated the composition of the adsorbate. They relied on the established fact that uncontaminated whale oils gave a pale product at the end of the test, even if the original oil were very dark, whereas contaminated oils always led to a dark extract. The meeting would appreciate the fact that the authors did not rely on any one indication of the presence of fuel oil, but based their conclusions on the sum total of the evidence that could be obtained.

A Method for the Routine Determination of Glycogen in Oysters

By JOHN P. TULLY

(*Read at the Meeting, November* 3, 1937)

It became necessary to develop a routine method for the determination of glycogen in oysters during a series of analyses of the Pacific coast species.

Pflüger's method of digestion, precipitation, purification and hydrolysis was adopted as a basis of procedure, and the possibility of using sodium hydroxide as a medium for digestion was studied; some of the many recent modifications suggested by Sayhun and Alsberg,[5] Good, Kramer, and Somogyi,[3] and Cori and Cori,[2] were also investigated under the following headings.

In every instance the glucose in the resulting solutions was determined by the Schaffer-Hartmann cuprous method,[6] with the modifications of Marsh and Joselyn,[4] and of Schaffer and Somogyi.[7]

1. *Time of digestion in a* 10 *N solution of sodium hydroxide and potassium hydroxide* (*Pflüger*).—A number of fresh oysters were finely minced and thoroughly mixed, and four aliquot portions were taken; two of these were digested in a 40 per cent. solution of sodium hydroxide and two in a 56 per cent. solution of potassium hydroxide (approximately 10 *N*) at 100° C. One portion of each digest was heated for three, and the others for six hours.

When cooled, all the digests were of an amber colour with a curd of black soap floating on the surface. The sodium hydroxide digests were darker and the soaps harder than those of the potassium hydroxide digest. The digests were diluted to twice their original volume, aliquot parts were withdrawn from each, sufficient ethyl alcohol was added to make the alcoholic strength 66 per cent., the whole was thoroughly mixed, and the precipitates were allowed to settle for 24 hours.

From the sodium hydroxide digests there was obtained a clear amber-coloured solution on top, and a black semi-liquid soap-like precipitate of impure glycogen at the bottom. The supernatant liquid was decanted through a No. 2 Whatman filter-paper with the aid of slight suction. No glycogen could be detected in the filtrate. The residue, on re-precipitation, yielded a yellowish flocculent precipitate of glycogen.

From the potassium hydroxide digest there resulted a layer of clear amber-coloured solution, and a grey-brown flocculent precipitate, which on re-precipitation, yielded pure white glycogen.

TABLE I

Digestion period Hours	Glycogen as dextrose: Sodium hydroxide digest Per Cent.	Glycogen as dextrose: Potassium hydroxide digest Per Cent.
3	15·5	19·8
6	15·5	19·8

The glycogen was then determined as dextrose, and, as shown in Table I, the yields from both potassium and sodium hydroxide digests were no greater after 6 than after 3 hours; consequently, 3 hours' digestion was adopted in all subsequent analyses.

(2) *Concentration of ethyl alcohol required for complete precipitation of glycogen.*[3]—Aliquot portions of each of the sodium and potassium hydroxide digests were diluted to twice their original volume, ethyl alcohol was added to give alcoholic strengths of 40, 50 and 66 per cent., the whole was thoroughly mixed, and allowed to settle for 24 hours, and the glycogen was then filtered off. In each instance the concentration of alcohol in the filtrate was increased to ascertain if unprecipitated glycogen was present. Identical results were obtained with the derivatives of both the sodium and the potassium hydroxide digests.

There was additional precipitation of glycogen in the filtrate from the 40 per cent. alcohol precipitation, when the concentration of alcohol was increased to 60 per cent., but none when the 50 per cent. filtrate was increased to 65 per cent., or the 66 per cent. to 75 per cent.

TABLE II

Concentration of ethyl alcohol Per Cent.	Glycogen as dextrose: Sodium hydroxide digest Per Cent.	Glycogen as dextrose: Potassium hydroxide digest Per Cent.
40	5·5	11·2
50	15·5	19·8
66	15·5	19·8

The glycogen was purified by re-precipitation and determined as before. On the basis of these results, as shown in Table II, a concentration of 55 to 60 per cent. of ethyl alcohol was adopted for the glycogen precipitation.

(3) *Advantage of heating the alcohol solution of the digest in order to hasten the precipitation of glycogen.*[2]—The efficacy of heating the alkali solution after the addition of the alcohol, as suggested by Cori and Cori,[2] was tested by treating two aliquot parts from each digest—one from each as described above (Section 2), and the other by heating to boiling in a water-bath. The glycogen, when heated, was precipitated as a gum-like substance which adhered to the sides of the vessel. The supernatant liquids, when decanted twice through a Whatman No. 2 filter-paper with the aid of slight suction, were perfectly clear, and gave no reaction for

glycogen. All the samples were re-precipitated as before, and the glycogen was determined.

TABLE III

Alcohol (55–60 per cent.) precipitation (state)	Glycogen as dextrose	
	Sodium hydroxide digest Per Cent.	Potassium hydroxide digest Per Cent.
Cold	15·5	19·8
Hot	15·5	19·8

As shown in Table III, both methods gave identical results; consequently, in further tests, the heating procedure was adopted, in order to hasten precipitation.

(4) *Concentration of hydrochloric acid and the time of digestion at* 100° C., *necessary for the complete hydrolysis of the glycogen.*[5]—Sayhun and Alsberg[5] show that complete hydrolysis is effected by heating the glycogen solution for 3 hours at 100° C. with 2·2 per cent. (0·6 *N*) hydrochloric acid, and in 2 hours with 3·65 per cent. (*N*) hydrochloric acid.

Concentrations of 1 per cent. (0·27 *N*), 3 per cent. (0·83 *N*), and 5 per cent. (1·38 *N*) hydrochloric acid were used for the hydrolysis of the glycogen solutions obtained from each digest, and the times of digestion were chosen as 1, 2, and 3 hours at 100° C. The results are shown in Table IV.

TABLE IV

Concentration of hydrochloric acid Per Cent.	Time of hydrolysis Hours	Glycogen as dextrose	
		Sodium hydroxide digest Per Cent.	Potassium hydroxide digest Per Cent.
1	1	7·16	16·9
3	1	13·5	19·9
5	1	19·1	24·5
1	2	11·9	23·0
3	2	13·5	24·5
5	2	11·1	24·5
1	3	11·9	23·7
3	3	15·1	26·1
5	3	15·9	26·1
3	5	—	26·0

It is assumed that the highest values for glycogen expressed as dextrose (26·1 per cent.) represent the most accurate results. For the temperature of digestion employed, namely, 100° C., it is shown that the largest yield of dextrose is obtained from the potassium hydroxide digest with 3 to 5 per cent. hydrochloric acid in 3 hours.

(5) *Tendency toward adsorption of the glycogen by the soaps formed during the digestion.*[1,8,9].—It is shown in Tables I, II, III, and IV that the yield of dextrose from the sodium hydroxide digestion is much less than that from the potassium hydroxide digest. This discrepancy is possibly due to the adsorption of glycogen on the sodium soap formed during the digestion. To determine the extent of such

adsorption, if any, a separate examination of the soap and the supernatant liquid was made in both digests. The results are shown in Table V.

TABLE V

	Glycogen as dextrose	
	Sodium hydroxide digest Per Cent.	Potassium hydroxide digest Per Cent.
Supernatant liquid	15·3	20·1
Black soap	6·8	20·1

This indicates that the glycogen is selectively dissolved in the supernatant liquid in the sodium hydroxide digest, or that glycogen is adsorbed on the soap, and in this state escapes hydrolysis.

Schöndorf[8] has shown that glycogen is readily adsorbed on the hydroxides of the heavy metals which occur in oysters, and states that for this reason determinations by Pflüger's method may be as much as 50 per cent. too low. Przylecki and Mazmiu[9] have shown that glycogen is adsorbed on fats and lecithin, and from this the conclusion may be drawn that colloidal glycogen may be readily adsorbed by the soap in the digest. Bancroft and Fry[1] have demonstrated that the extent of hydrolysis depends on the amount of unadsorbed glycogen, and is independent of a large excess of either acid or glycogen, and the results they present are very similar to those shown in Table V.

When potassium hydroxide is used there is apparently no difference in the concentration of glycogen in any part of the digest; hence this reagent was adopted, and the aliquot portions for routine analyses were drawn from the supernatant liquid merely to simplify the purification procedure.

(6) *Necessity of filtering the glucose solution before determination.*—When the glucose solution obtained from the acid hydrolysis of the glycogen is neutralised, a dark flocculent precipitate is formed. The dextrose in a neutralised solution derived from the potassium hydroxide digest was determined in two aliquot parts, only one of which was filtered.

The filtered sample yielded 20·7 per cent., and the unfiltered sample 19·9 per cent. of dextrose; this demonstrates that the precipitate interferes with the determination of dextrose.

(7) *Use of dextrose for the standardisation of the sodium thiosulphate solution in the Schaffer–Hartmann sugar determination.*[6]—In the determinations of dextrose on the macro scale by the Schaffer–Hartmann cuprous method,[6] copper is used for the standardisation of the sodium thiosulphate solution. A comparison was made with the use of dextrose for standardisation.

The amount of dextrose in a sample of "Difco" standardised anhydrous dextrose was determined in the prescribed manner. Corrections for the impurities stated to be present in the dextrose were made in the weight taken, and the normality of the sodium thiosulphate solution was calculated.

This normality was 0·1526 and, found by means of copper, it was 0·1528, from which it is evident that either substance is suitable for this standardisation.

PROCEDURE ADOPTED.—On the basis of the foregoing investigation, the

following procedure was adopted for the routine determination of glycogen in oysters.

Preparation of the sample.—Shell and drain a number of oysters sufficient to give a suitable quantity of the moist meat. Mince finely, including any liquor that is ground out of the oysters, mix and sample the resultant mass.

Digestion.—Weigh 20 g. of the wet sample into a 200-ml. Berzelius beaker provided with a cover and stirring rod, add 40 to 50 ml. of hot 56 to 60 per cent. potassium hydroxide solution and digest, with frequent stirring, in a boiling water-bath for 3 hours.* Cool, and dilute the digest to 100 millilitres.

Precipitation.—Withdraw 50 ml. of the amber-coloured liquid, neglecting the black soap, into a 200-ml. Berzelius beaker, add 80 ml. of 95 per cent. ethyl alcohol and stir well. Heat in a water-bath (about 80° C.) until the alcohol in the mixture begins to boil. The precipitated glycogen adheres to the sides of the beaker. Decant the supernatant liquid through a No. 2 Whatman filter-paper under slight suction, repeating, if necessary, until the filtrate is bright and clear.

Purification.—Re-dissolve the crude glycogen in 50 ml. of boiling water and re-precipitate. This second precipitate should be quite white in an almost colourless liquid. Heat as before in the water-bath, and decant the supernatant liquid through the same filter. Wash the paper into the beaker with boiling water and re-dissolve the pure glycogen, making the solution up to 100 ml. (approximately). The glycogen solution, when cool, should be opalescent and of a very light buff colour.

Hydrolysis.—Add 8·5 to 11 ml. of conc. hydrochloric acid (10 *N*), making the solution 3 to 4 per cent. with respect to the acid, and digest in a boiling water-bath for 3 hours. Cool, add a drop of 2 per cent. phenolphthalein solution to the dextrose solution, and add conc. potassium hydroxide solution until a pink colour is just perceptible. Filter with the aid of slight suction, wash with boiling water, and make the filtrate up to 250 ml. The dextrose solution should be bright, clear, and of a very light buff colour (or pink, owing to the phenolphthalein).

Determination.—The dextrose may now be determined by any of the standard methods. If the Schaffer–Hartmann procedure[6] is adopted, the sodium thiosulphate solution may be standardised with copper, or with pure dextrose, as described.

After this work had been completed my attention was drawn to the investigations of Stubbs, More and Nicholls, of the Government Laboratory, London, who devised a technique for applying Pflüger's test to oysters.[10]

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* No reflux condenser is required, as the concentrated alkali will absorb enough water from the steam of the water-bath to keep the volume approximately constant.

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DISCUSSION

Mr. J. R. NICHOLLS remarked that all the methods for the determination of glycogen that had been published were based on Pflüger's classical work. This paper applied it to oysters, but it was not the first occasion on which that had been done. In 1920 Dr. Russell, of the Ministry of Agriculture and Fisheries, undertook an investigation into seasonal variations in the composition of oysters, and later Dr. J. H. Orton, of Liverpool, investigated the cause of the unusual mortality among oysters in 1920 and 1921. The chemical work was carried out at the Government Laboratory by Stubbs, More and Nicholls (the speaker), and was included in the Reports* published by the Ministry of Agriculture and Fisheries in 1923 and 1924. For the determination of glycogen they had modified Pflüger's method,† and in every essential it was practically the same as that described in the present paper. He thought that it was an advantage that this work should be published in THE ANALYST which had a wider circulation than the Reports of the Ministry.

He then described the results of their work and said that they were the first to point out the necessity of determining glycogen on the fresh oyster immediately after opening. If oysters were dried to a powder, as was usual when a complete analysis was required, about one-half of the glycogen was lost. This was now known to be due to lactic acid formation and not to hydrolysis to dextrose. The details of the method used were as follows:

DETERMINATION OF GLYCOGEN.—Three to five g. of the air-dried flesh were placed in an Erlenmeyer flask and heated in a boiling water-bath, with occasional shaking, for 3 hours, with 50 ml. of 60 per cent. potassium hydroxide solution. After cooling, the solution was diluted with water to about 100 ml., and 200 ml. of industrial methylated spirit were added gradually with continuous shaking. For the direct determination, the moist flesh, weighing from 40 to 90 g., was heated, as described above, with 100 ml. of 60 per cent. potassium hydroxide solution for 3 hours and made up to 250 ml., and 100 ml., in duplicate, were treated with alcohol. After standing overnight, the precipitated glycogen was filtered off on filter-paper in a Buchner funnel with the aid of a water-pump and washed successively with 200 to 300 ml. of 60 per cent. alcohol, 100 to 200 ml. of 95 per cent. alcohol, a little absolute alcohol, and 50 to 100 ml. of ether. Most of the glycogen was transferred back to the precipitating flask, and covered with cold water, and the remainder was washed in with warm water. When all had dissolved the solution was transferred to a graduated flask and made up to 200 or 250 ml. Fifty ml. (or 100 ml.) of this crude glycogen solution were diluted to about 120 ml., and heated in a boiling water-bath for 3 hours with 7·5 ml. of concentrated hydrochloric acid, and, after cooling, the solution was neutralised with sodium hydroxide solution and made up to 150 ml. The dextrose was determined in 50 ml. of the filtered liquid by means of Fehling's solution, and the glycogen was calculated by multiplying the total dextrose by 0·927. As a check determination, 25 ml. of the filtered crude glycogen solution were just acidified with acetic acid, two volumes of industrial methylated spirit were gradually added, and, after standing a few hours, the precipitated glycogen was filtered off on a Gooch crucible, washed with alcohol and ether, dried at 100° C. and weighed. After the glycogen had been burnt off the crucible was again weighed, the difference representing glycogen. This figure was invariably slightly higher (average about 3 per cent. of the glycogen) than that obtained by hydrolysis and was only regarded as a check figure.

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* "Report on Seasonal Variations in the Chemical Composition of Oysters." *Ministry of Agriculture and Fisheries, Fishery Investigations*, Series II, Vol. VI, No. 1, 1923.
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† Report No. 4, p. 61.

The Excretion of Sodium Cyanide when administered Intravenously in Small Doses

By G. V. JAMES, M.Sc., F.I.C.

In the course of an investigation into circulatory rate, during which sodium cyanide was used to stimulate the respiratory centre, the opportunity arose of examining the urine in several cases for the presence of cyanide, with the object ot determining its fate—a point on which there is controversy.

Sollman[1] considers that hydrocyanic acid is unstable and rapidly changes. Part of it combines with sulphur to produce thiocyanates and a portion is excreted unchanged by the lungs. The fate of the remainder is unknown. Thiocyanate occurs in parotid saliva, urine and (in traces) in the stomach. Klaassen[2] confirms this and criticises the results of Schechter[3] on the ground that the latter used abnormal cyanide concentrations in relation to the liver tissue.

Sollis Cohen and Gittens[4] are of opinion that sodium cyanide is excreted as hydrocyanic acid in the breath and as cyanide in the urine. In the opinion of Autenrieth[5] part passes unchanged by the lungs, and a smaller part passes through the kidneys to the urine; sweat is said to contain hydrocyanic acid. He considers cyanhydrin and thiocyanate formation as possibilities, as well as hydrolysis to ammonium formate and oxidation.

A fresh 2 per cent. solution of sodium cyanide, in doses of 0·11 mg. per kg. of body weight, is injected into the antecubital vein; when the drug reaches the carotid sinus an increase in the amplitude of respiration is produced. The quantities used are non-toxic and the effects quickly pass off, respiration becoming normal in about 30 seconds. The dose can therefore be repeated at frequent intervals, although when this has been done a number of times in succession early toxic symptoms appear.[6]

The cyanide was estimated in the specimens by the method of Pagel and Carlson,[7] a measured quantity of the sample being acidified with dilute sulphuric acid, brought to distillation temperature within 5 minutes, and distilled for about 20 minutes, the distillate being collected in dilute sodium hydroxide solution.

The presence of cyanide in the distillate was first confirmed by the silver nitrate, the Prussian blue and the thiocyanate tests. It was determined colorimetrically by means of the guaiacum-copper and alkaline picrate method of Autenrieth[5] and the benzidine-copper method adapted from that mentioned by Davidson Pratt.[8]

Briefly, the distillate is made faintly acid with acetic acid, to about *p*H 4–*p*H 5, and divided into three portions:

(1) This portion is treated with 10 ml. of saturated picric acid solution, allowed to stand for 5 minutes, then treated with 5 ml. of 10 per cent. sodium hydroxide solution, left for 15 minutes, and diluted to 100 ml. A standard for comparison is treated similarly.

(2) The second portion is treated with 5 ml. of a freshly-prepared 5 per cent. alcoholic tincture of guaiacum and 0·1 ml. of 1 per cent. copper sulphate, solution and diluted to 100 ml. with 50 per cent. alcohol; a standard is similarly treated.

(3) Finally to the third portion of the distillate, 10 ml. of the benzidine-copper reagent are added and the mixture is diluted to 100 ml. and matched with a standard. The reagent is made by mixing 25 ml. of 1 per cent. benzidine acetate solution with 5 ml. of 3 per cent. copper acetate solution.

A table is appended giving examples of results obtained on the same distillate by the three different methods.

	Sodium cyanide found		
Distillate	Alkaline picrate method mg.	Guaiacum-copper method mg.	Benzidine-copper method mg.
1	0·97	1·05	1·08
2	0·75	0·78	0·775
3	0·90	0·89	0·87
4	0·75	0·77	0·73
5	1·22	1·20	1·19

I prefer the benzidine-copper method, as with this it is possible to obtain a null-colour (not possible with the picrate method), and there is not likely to be separation of resinous substances (as may occur with the guaiacum-copper method).

The methods cannot be directly applied to urine owing to the presence of creatinine (affecting the picrate) or of enzyme of the oxidase type affecting both copper methods. As traces of urine tend to froth over during the distillation and so affect the result, I have found it useful to add a little liquid paraffin or amyl or capryl alcohol to prevent this.

In certain cases, tests for the presence of thiocyanate were made on urines, both before and after doses of cyanide, but with negative results. Excess of ferric chloride solution was added, and the urine was extracted with amyl alcohol or ether; no colour was developed. Addition of calcium chloride, prior to the iron, to remove phosphates, did not, in any instance, result in a positive reaction for thiocyanate being obtained.

One urine gave an abnormally high result, and this led to a consideration ot dietary factors, as it was found that cabbage had been eaten at a previous meal; it is known that nitriles occur in cabbage.[10] Accordingly, urines were collected from people who had partaken of cabbage or Brussels sprouts at a meal and the cyanogen was estimated. The results, given in Table I, were obtained in the examination of the urine 3½ hours after the meal. In every case the urine before the meal was free from cyanide. In all subsequent experiments, no patient who had partaken of a cruciferous plant at a previous meal was examined. Further investigations are being carried out on these foodstuffs.

TABLE I

		Vol. of urine ml.	Cyanogen as sodium cyanide mg.
Cabbage:	Case 1	397	8·6
	Case 2	410	4·0
	Case 3	160	1·64
Sprouts:	Case 1	510	9·3
	Case 2	290	6·7

The quantity of cyanide present at the end of various time-intervals after injection was determined in three cases, and the results (Table II) indicate that an interval of 30 minutes is ample for collection of the urine.

TABLE II

	Collection of urine		Sodium cyanide excreted	
	Time interval Minutes	Vol. of urine ml.	Amount mg.	Per cent. excreted
Case 1:	30	60	1·08	18
	30–60	55	0·18	3
	60–90	50	0·0	0
Case 2:	30	38	0·9	15
	30–60	26	0·11	1·8
	60–90	33	0·04	0·7
Case 3:	30	61	0·9	18
	30–60	65	0·06	1·3
	60–90	317	0·045	0·9

Six mg. of sodium cyanide were given in cases 1 and 2, and 5 mg. in case 3. To ensure standard conditions, in each case a request was made that the bladders should be emptied before the experiment began.

The percentage of cyanide voided in the urine was remarkably constant, and the results could be duplicated when the same case was examined with an interval of a day or so after each injection (Table III).

TABLE III

	6 mg. dose given in each case		
	Volume of urine ml.	Sodium cyanide excreted mg.	Per cent. excreted
Case 1:	66	0·99	16·5
	60	1·08	18·0
Case 3:	134	0·90	15·0
	95	1·07	17·9
Case 4:	38	0·90	15·0
	30	1·07	17·9
Case 8:	38	1·00	17·0
	15	1·08	18·0
Case 20:	83	1·20	20·0
	29	1·20	20·0
Case 21:	33	1·16	19·3
	23	1·20	20·0

The effect of varying the dosage of cyanide was investigated in three cases, and it was found (Table IV) that for a particular person the percentage excretion was approximately constant.

In one case, about 5 minutes after injection, a cyanide flavour was noticed in the mouth, and the saliva secreted during the period was therefore kept and examined for cyanide; it was found to be present to the extent of 1·10 mg. or

14·0 per cent. In three other cases, remarks were made on the characteristic flavour.

TABLE IV

	Volume of urine	Dose of sodium cyanide mg.	Sodium cyanide excreted mg.	Per cent. excreted
Case 1:	24	4	0·75	19·1
	60	6	1·08	18·0
	37	8	1·50	19·0
Case 2:	84	4	0·775	19·4
	61	5	0·90	18·0
	140	6	1·05	17·5
Case 24:	115	6	1·50	25·0
	80	7	1·70	24·3

The same percentage of sodium cyanide appears to be excreted by normal cases and pathological heart cases in the same time, as is shown in Table V.

TABLE V

Case	Condition	Dose mg.	Vol. of urine in 30 minutes ml.	Sodium cyanide excreted mg.	Per cent. excreted	Mg. of Cyanide per 100 ml.
1.	Normal	6	66	0·99	16·5	1·5
		6	60	1·08	18·0	1·8
2.	,, ...	6	140	1·05	17·5	0·75
4.	Auricular fibrillation ..	6	38	0·90	15·0	2·4
		6	30	1·07	17·9	3·6
5.	Aortic stenosis ..	6	34	0·88	14·7	2·3
6.	Myocardial degeneration	6	26	0·70	11·7	2·7
7.	Auricular fibrillation ..	6	28(1hr.20m.)	0·74	12·3	1·0
8.	,, ,, ..	6	38	1·00	17·0	2·1
		6	15	1·08	18·0	7·2
9.	Cardiac asthma ..	6	21	1·09	18·2	5·2
10.	Coronary thrombosis ..	6	31	1·31	22·0	4·2
11.	Myocardial degeneration	6	26	0·90	15·0	3·5
12.	,, ,, ..	6	36	1·42	23·7	4·0
13.	Mitral stenosis	6	45	1·20	20·0	2·7
15.	Hyperpiesia	8	18	1·60	20·0	8·8
16.	Mitral stenosis	6	64	0·95	15·9	1·5
17.	Thyrotoxicosis	6	55	1·07	17·9	2·0
18.	Hyperpiesia	6	34	0·75	12·5	2·2
19.	Auricular fibrillation ..	8	25	1·60	20·0	6·4
20.	Thyrotoxicosis	6	83	1·20	20·0	1·4
		6	29	1·20	20·0	4·0
21.	Congestive failure ..	6	33	1·16	19·3	3·5
		6	23	1·20	20·0	5·2
22.	Brachycardia	6	113	0·99	16·5	0·9
23.	Thyrotoxicosis	8	29	1·70	21·1	6·0

It will be seen that the quantity of cyanide is dependent on the volume of urine, and hence an increased percentage output might be expected after administration of a diuretic. That this occurs is shown in Table VI.

TABLE VI

		No. diuretic				Diuretic present		
Case	Dose	Vol. of urine ml.	Sodium cyanide excreted mg.	Per cent. excreted	Diuretic	Vol. of urine ml.	Sodium cyanide excreted mg.	Per cent. excreted
4.	6	38	0·9	15·0	Salyrgan	269	3·25	54·2
8.	6	38	1·00	17·0	Diuretin	46	1·66	27·7
19.	8	25	1·6	20·0	Salyrgan ..	160	4·8	60·0
	7				Ammonium chloride	84	5·44	78·0*
24.	6				Water	115	1·5	25·0
	7				,, ...	80	1·7	24·3
25.	8				Ammonium chloride	25	2·0	25·0
19.	8				Salyrgan ..	137	2·17	26·4

* No respiratory reaction.

The distribution between urine and breath was investigated in one case by causing the patient to breathe through a mask into a 1 per cent. solution of sodium hydroxide and estimating the quantity of cyanide present after 30 minutes. Owing to the inconvenience it caused the patient, the method could not be applied in other cases, but the excretion by the lungs was checked by use of a copper-benzidine test-paper, which showed that the cyanide was excreted mainly in the early stages of the reaction.

TABLE VII

Sodium cyanide injected, 6 mg.

Cyanide excreted:

In the breath	4·5 mg. (as NaCN)	=	75·0 per cent.
In the urine	0·75 mg. ,, ,,	=	12·5 ,,
			87·5

In every instance the urine was examined for cyanide before the injection, and in no case could it be detected.

SUMMARY.—Cyanide given intravenously is rapidly excreted in the urine and breath, the major part apparently coming through the lungs. The amount in the urine is affected by the use of diuretics.

I wish to thank Dr. R. W. Eason, M.D., M.R.C.P., for putting patients at my disposal and providing specimens to enable me to do this work.

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August, 1937

The Electrical Deposition and Determination of Arsenic

BY SYDNEY TORRANCE, A.R.C.S., B.Sc., D.I.C.

ARSENIC, when present in small quantities, may be determined electrolytically by reduction to arsine with nascent hydrogen in the electrolytic Marsh test. The original methods were due first to Bloxam,[1] then later to Thorpe,[2] Sand and Hackford,[3] and Trotman.[4] Ramberg[5] concluded that mercury was the most effective metal to use as the cathode for this reduction. Aumonier[6] modified and improved Ramberg's method, and this latter method is the present standard method for the electrolytic determination of small amounts of arsenic.

The actual deposition of arsenic as the metal presents many difficulties. A direct quantitative deposition has not yet been performed. Arsenic does not deposit from arsenates nor from arsenites in nitric or sulphuric acid solutions. It may be deposited from a strong hydrochloric acid solution of an arsenite, but the deposition is not quantitative. The cathode potential must be carefully controlled and not allowed to rise too high, as any hydrogen liberated would immediately convert the arsenic into gaseous arsine.

Arsenic is deposited together with antimony and tin, and it had been previously found[7] that it was deposited with copper from a strong hydrochloric acid solution, in the electrolytic equivalent of the Reinsch test. This property was investigated further, and a method worked out for the quantitative deposition and determination of arsenic.

Important papers on the mechanism of the Reinsch test were published in 1923 by B. S. Evans,[8] who adduced that the presence of the chloride ion was necessary for this test. As an introduction to the present investigation an examination of the Reinsch test was first carried out, in different acid media, and under different conditions of acid concentration and temperature. The test solutions, in boiling-tubes, contained 0·05 g. of anhydrous sodium arsenite or arsenate, and were made up to the different acid concentrations, by addition of the requisite amounts of

concentrated acid. The volume of each solution was 20 ml. A piece of clean copper foil was added to each solution, and the boiling-tubes were placed for 10 minutes in a water-bath at 50° C. The tubes in which no positive results were thus obtained were placed in a steam-bath for a further ten minutes. The contents of such boiling-tubes as still showed no positive reaction were boiled for five minutes longer. The following results (Table I) were obtained:

TABLE I

	Arsenite solution			Arsenate solution		
Acid medium	Water-bath at 50° C.	Steam-bath	Boiled	Water-bath at 50° C.	Steam-bath	Boiled
2 *N* Sulphuric acid	Negative	Negative	Negative	Negative	Negative	Negative
5 *N* ,,	,,	,,	Very slight	,,	,,	,,
10 *N* ,,	,,	Slight	Definite	,,	,,	,,
20 *N* ,,	,,	Definite	Positive	,,	,,	,,
2 *N* Nitric acid	,,	Negative	Negative	,,	,,	,,
5 *N* ,,	,,	,,	,,	,,	,,	,,
N Hydrochloric acid	Positive	—	—	,,	,,	Positive
2 *N* ,,	,,	—	—	,,	,,	,,

A standard solution of tervalent arsenic was prepared by dissolving arsenious oxide in 5 per cent. hydrochloric acid. Fifteen ml. of hydrochloric acid (sp.gr. 1·16) were added to a portion of the standard solution equivalent to 5·0 mg. of arsenic, and the mixture was diluted to 150 ml. One g. of hydrazine hydrochloride was added,* and the mixture was electrolysed for 15 to 20 minutes, at 50° C., between platinum gauze electrodes. The auxiliary cathode potential was maintained at 0·4 volt, a Sand saturated calomel electrode[9] being used. The initial current was 0·4 amp., and fell rapidly to below 0·1 amp. The weight of arsenic deposited was 0·9 mg., equivalent to 18 per cent. of the amount added. A repetition gave a similar result, although the deposition was continued for one hour.

The electrolysis was then repeated with the addition to the electrolyte of 25 ml. of a standard (1 per cent.) copper solution (as copper sulphate). The initial current rose to about 4 amps., but again fell rapidly, within ten minutes, to about 0·1 amp. When the current was at a minimum the electrolysis was continued for a further five minutes. The liquid in the tip of the auxiliary electrode vessel was flushed into the main electrolyte, and the deposition was continued for five minutes longer. The auxiliary potential was maintained throughout at 0·4 volt. All the copper and all the arsenic were thus deposited together. This was confirmed by dissolving the weighed deposit in a mixture of 5 ml. of sulphuric acid (sp.gr. 1·82), 5 ml. of nitric acid (sp.gr. 1·42), and 10 ml. of water, boiling off oxides of nitrogen, diluting to 150 ml., adding 1 g. of hydrazine sulphate, and electrolysing for twenty minutes at 50° C. with an auxiliary potential of 0·4 volt. Copper only was deposited, and the weight of deposit was equal to the amount of copper originally added as copper sulphate. The difference in weight between the two deposits was equal to the weight of arsenic originally taken. This latter

* Repeated experiments have shown that the addition of hydrazine hydrochloride is effective in preventing attack on the anode.

electrolysis was repeated with varying amounts of arsenic. The deposition of arsenic was quantitative for amounts of arsenic below 0·05 g. When the weight of arsenic in the electrolyte was 0·05 g. or more, all the arsenic did not come out with the copper. On re-electrolysing the residual solution with a further 25 ml. of the copper solution, the remainder of the arsenic was deposited. The results are shown in Table II.

TABLE II

Arsenic taken g.	Copper added g.	Copper and arsenic deposited g.	Arsenic found g.	Total arsenic deposited g.
*0·0050	—	0·0009	0·0009	
*0·0050	—	0·0009	0·0009	
*0·0050	0·2409	0·2460	0·0051	
*0·0050	0·2409	0·2459	0·0050	
0·0050	0·2409	0·2460	0·0051	
*0·0100	0·2409	0·2511	0·0102	
0·0100	0·2409	0·2510	0·0101	
0·0250	0·2409	0·2659	0·0250	0·0250
* —	0·2409	0·2409	—	
0·0500	0·2409	0·2866	0·0457	0·0503
—	0·2409	0·2455	0·0046	
*0·0500	0·2409	0·2861	0·0452	0·0502
* —	0·2409	0·2459	0·0050	

In the experiments marked * the amount of copper added was confirmed by dissolving the combined deposit in the solvent mixture mentioned above, and re-depositing the copper.

A standard quinquevalent arsenic solution was prepared by dissolving anhydrous sodium arsenate in water. An aliquot portion was electrolysed as described above, in 10 per cent. hydrochloric acid solution, with copper. All the copper was deposited, but no arsenic. A further aliquot portion was made just acid with sulphuric acid, and reduced by boiling for 5 to 10 minutes with 5 ml. of saturated sulphurous acid solution. This solution was then electrolysed in the usual way with hydrochloric acid, copper and hydrazine hydrochloride, for twenty minutes at 50° C., with an auxiliary potential of 0·4 volt. The arsenic was quantitatively deposited with the copper. Table III gives the results.

TABLE III

Arsenic taken g.	Copper added g.	Copper and arsenic deposited g.	Arsenic found g.
0·0100	0·2409	0·2508	0·0099
0·0100	0·2409	0·2507	0·0098
0·0250	0·2409	0·2657	0·0248
0·0250	0·2409	0·2667	0·0248

I wish to thank Dr. Sand for his interest in this work.

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May 27th, 1937

A Rapid Method for the Determination of Bismuth in Copper, Brasses, Bronzes, etc.

BY H. R. FITTER

IN most methods used for the colorimetric determination of bismuth in brasses and bronzes by the formation of bismuth iodide, the operations preceding the final separation of bismuth are long and tedious, and there is also danger of incomplete separation of the bismuth itself. This is especially so when tin is present in the sample. In some modern specifications for gunmetal it is stated that the bismuth-content must be less than 0·01 per cent.; hence the necessity for a very accurate method of analysis, that can also be made quickly when many samples have to be dealt with.

Experiments have shown that if copper, or copper alloys, such as brass, bronze, gunmetal, and the like, are dissolved in a mixture of hydrochloric and nitric acids, and the solution is neutralised with ammonia, then acidified with sulphuric acid and treated with sufficient potassium iodide to precipitate the copper, and if then the liberated iodine is reduced by addition of a solution of either sodium thiosulphate or sulphurous acid and the resultant solution filtered, the filtrate will contain, in the form of the characteristic yellow bismuth iodide, the whole of the bismuth present in the sample. The bismuth may then be determined by matching the colour against a standard solution of bismuth iodide, provided that the colour of the solution under examination remains unchanged. If sodium thiosulphate has been used, a precipitate of sulphur quickly forms, and this makes a good colour match impossible. If a solution of sulphurous acid has been used (which must necessarily have been a comparatively strong one) the excess of sulphur dioxide reacts with the potassium iodide in the solution to form a colour identical with that of bismuth iodide, and thus tends to give high results. This difficulty was experimentally overcome by the following procedure:

After the precipitated copper iodide had been filtered off the excess of sulphur dioxide was oxidised by the addition of $N/10$ permanganate solution until a brown colour, due to liberated iodine, was just obtained; this brown colour was then destroyed by the addition of a very dilute solution of sulphurous acid, only one or two drops in excess being used. A fine adjustment with these two reagents gave a solution in which a very accurate colorimetric determination of the bismuth could be made. As, however, the solution under examination gradually altered

in colour, owing either to the reaction of sulphur dioxide and potassium iodide or to atmospheric oxidation, it was found necessary to make continual adjustments during the matching of the colours. This method cannot therefore be recommended as entirely satisfactory.

Experiments were then made in which sodium hypophosphite was used to reduce the iodine liberated after the addition of potassium iodide, and it was found that this gave excellent results, and that the solutions so obtained could be kept for several days without alteration in colour.

METHOD.—The details of the method finally adopted are as follows:—Dissolve 2 g. of the sample in a mixture of 14 ml. of dilute (1 : 1) hydrochloric acid and 6 ml. of nitric acid (sp.gr. 1·2) in a 250-ml. tall beaker and heat gently. Wash down the sides of the beaker and, without further dilution, add dilute ammonia solution (1 : 1) until the solution is distinctly alkaline. Next add dilute (1 : 3) sulphuric acid until a clear solution is just obtained, and then add 10 ml. in excess. Cool, and add an excess of a 60 per cent. solution of potassium iodide to precipitate the copper (6 g. of potassium iodide for each 1 g. of copper). Next add 5 g. of sodium hypophosphite dissolved in 20 ml. of water. Thoroughly mix and allow the solution to stand until completely bleached; this will take about 10 minutes. Transfer the solution to a measuring cylinder and dilute to exactly 200 ml. Filter off 100 ml. of the solution, representing 1 g. of the sample If any bismuth is present, it will now be seen as the yellow iodide. Transfer the solution to one of a pair of matched 100-ml. Nessler tubes; in the other Nessler tube put 5 ml. of dilute (1 : 3) sulphuric acid, 1 g. of potassium iodide and 1 g. of sodium hypophosphite and dilute the solution to a few ml. short of the graduation mark. Into this tube run standard bismuth sulphate solution (1 ml. ≡ 0·0001 g. of bismuth) until the colours match when the solution is diluted to the graduation mark. If the colour is too deep for comparison, divide the sample solution and dilute it.

RESULTS.—The following results were obtained with samples prepared by dissolving mixtures of:

Pure copper ..	1·75 g.	≡	87·5 per cent.
Pure tin	0·20 g.	≡	10·0 ,, ,,
Pure zinc	0·04 g.	≡	2·0 ,, ,,
Lead (as nitrate) ..	0·01 g.	≡	0·5 ,, ,,

representing a typical gunmetal containing lead. Varying amounts of bismuth sulphate were added to the beakers containing the above mixture as shown below.

Sample No.	Bismuth added Per Cent.	Bismuth found Per Cent.
1	None	None
2	0·0075	0·0075
3	0·015	0·0155
*4	0·05	0·049
5	0·019	0·0195
6	0·012	0·013
†7	0·019	0·0185
8	0·001	0·001
9	0·003	0·003

* The solution had to be halved, as the colour was considered too deep for comparison.

† To this sample was added lead nitrate representing 3 per cent. of lead, and the copper content was reduced by a like amount.

To three other samples, prepared as described above, without the addition of bismuth, there was added the equivalent of 2 per cent. of iron to one, of 0·2 per cent. of antimony to another, and of 0·5 per cent. of arsenic to the third. In each instance the method gave a perfectly colourless solution.

Two portions of a sample of copper nickel alloy were taken which gave the following composition on analysis:—copper, 28·27; nickel, 68·67; iron, 1·54; aluminium, 0·37; manganese, 1·06 per cent.

To one portion was added standard bismuth solution equivalent to 0·01 per cent. of bismuth, and none to the other. On testing for bismuth by the method described above, the green colours of the solutions obtained were appreciably different in shade, but matched exactly when standard bismuth solution, representing 0·01 per cent. of bismuth, was added to the solution containing no added bismuth.

A large number of samples of copper, brasses, bronzes, and the like have been examined for bismuth by this method and no difficulties have been encountered. When the sample is in the form of drillings or filings an analysis can be completed within an hour.

Investigations on the application of the method to the determination of bismuth in tin, zinc and alloys of these metals are being made.

I wish to acknowledge my indebtedness to the Admiralty for permission to publish this method.

DEPARTMENT OF THE ADMIRALTY CHEMIST
H.M. DOCKYARD, PORTSMOUTH
August 21st, 1937

Erratum.—ANALYST, 1937, **62**, p. 257, Table VI : The heading should read as follows :

APPROXIMATE WEIGHT PRODUCTION OF MILK FATTY ACIDS IN COWS RECEIVING 4 OZS. DAILY OF COD-LIVER OIL IN FOOD

(Combined milk from 2 cows collected over 4-day periods in each case)

In the first line of the Table, *for* "Milk-fat production per day" *read* "Milk-fat production over 4-day period."

Notes

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

THE DETERMINATION OF COPPER, ANTIMONY, MAGNESIUM AND TIN IN SPECIAL ALUMINIUM ALLOYS

THE following rapid method is used in this laboratory:—*Antimony.*—Two g. of the alloy millings are dissolved in 45 ml. of 12·5 per cent. sodium hydroxide solution, the solution is treated, while boiling, with about 3 g. of sodium peroxide (0·5 g. at a time), and the boiling is continued for 10 minutes. The liquid is filtered immediately through a hard (Whatman No. 541) filter-paper, and the residue (*a*) is washed and reserved.

The filtrate is treated with 75 ml. of hydrochloric acid (sp.gr. 1·16), with stirring, then heated, and when clear evaporated to crystallisation with a few crystals of potassium chlorate. It is then cooled, transferred to a 500-ml. Erlenmeyer flask, diluted to 200 ml., and, after the addition of potassium iodide titrated with $N/20$ sodium thiosulphate solution.

Copper.—The insoluble residue (*a*) is dissolved in nitric and hydrochloric acids, and the solution is boiled to expel nitrous fumes, then cooled, treated with ammonium hydroxide until the precipitated copper re-dissolves, warmed and filtered. The filtrate and washings are made up to 250 ml., and divided into two equal portions (*b*) and (*c*).

Solution (*b*) is slightly acidified with acetic acid, a few grams of potassium iodide are added, and the liberated iodine is titrated with $N/20$ sodium thiosulphate solution, starch being used as indicator.

Magnesium.—The solution (*c*) is treated with dilute (1:1) hydrochloric acid until just acid and neutralised with ammonia. Six g. of sodium acetate and 12 ml. of glacial acetic acid are added, and the liquid is warmed to 60° C. and treated with an excess (25 ml.) of a 2 per cent. alcoholic solution of 8-hydroxyquinoline. After standing for 15 minutes in a warm place the precipitate (copper) is filtered off.

The filtrate is warmed to 65° C. and made alkaline with ammonia. The precipitated magnesium quinolate is left for 15 minutes in a warm place, filtered off, washed thoroughly with boiling water, and dissolved in 200 ml. of 2 N hydrochloric acid, and a known excess (*e.g.* 20 ml.) of $N/10$ bromide bromate solution is added. About 3 g. of potassium iodide are added, and the liberated iodine is titrated with $N/10$ sodium thiosulphate solution.

Tin.—Two g. of the alloy and 0·5 g. of pure powdered antimony are treated with dilute (1:1) hydrochloric acid in a 500-ml. Erlenmeyer flask fitted with a rubber stopper and a delivery tube dipping into a saturated solution of sodium bicarbonate, the initial vigour of the reaction being controlled by placing the flask in a cooling bath. Finally, the liquid is boiled for 10 minutes, and cooled to room temperature (with the delivery-tube still dipping into the bicarbonate solution). By drawing back the bicarbonate solution an atmosphere of carbon dioxide is generated in the flask during cooling. When cold, the solution is treated with 2 g. of potassium iodide and 5 ml. of starch solution, and titrated with standard iodate solution (1·8 g. of potassium iodate and 2 g. of sodium hydroxide per litre; standardised on pure tin). The result of a blank determination is deducted.

This note is published because it was considered desirable that any modern

analytical procedures used in the control of a specific industrial product should be universally available.

We wish to acknowledge our indebtedness to the British Aluminium Company, Ltd., for permission to publish the work.

G. B. BROOK
G. H. STOTT
A. C. COATES

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THE ACTION OF MOULDS ON INK IN WRITING

A FEW months ago the manufacturers of a blue-black writing ink received a complaint that writing in this ink on parchment documents had faded to a yellowish-brown. The documents, which were about two years old, had been kept in a safe, and it was stated that writing in the same ink on paper or imitation parchment documents kept under the same conditions showed no signs of fading.

Examination of one of the parchment documents confirmed the complaint. The aniline dye in the blue-black ink had been completely bleached and the iron tannate had been decomposed, leaving a brownish-yellow residue of iron oxides. The violet aniline dye in some typing on the document had also been bleached in places, but the drawing of a plan in Indian ink (with a carbon basis) had not been affected. The document was damp and had a very mouldy odour and discoloured patches of mould were obvious. When the parchment was left in contact with moist lead acetate paper a slight brownish stain was produced on the paper.

These facts suggested that the fading of the writing ink was caused by the action of moulds. Accordingly, a hard-boiled egg was partly shelled and the white was inoculated with moulds from the surface of the parchment. After two days' incubation there was a vigorous growth, and, from this, cultivations were made on nutrient gelatin. Two species of moulds—*Penicillium* and *Aspergillus*—were thus isolated. The *Penicillium* species was found to belong to the sub-group that liquefies gelatin and evolves a considerable amount of ammonia. It did not evolve hydrogen sulphide or other volatile sulphur compound capable of combining with lead acetate to form lead sulphide; hence the stain produced on lead acetate paper by the parchment must have been due to decomposition of the copperas in the ink and not to decomposition of the protein in the parchment.

To test the combined action of the two moulds on inks, some words were written in blue-black ink on strips of another parchment (not infected with mould), and the moulds were implanted on these in a moist Petri dish and allowed to grow for two weeks at 21° C. The ink had then become much fainter and browner than that on another strip of the experimental parchment, which had been kept as a control. It is well known that ammonia will cause writing ink to fade and turn brown, and the experiments described afford an explanation of the fading of the ink on the parchment document.

We are indebted to Mr. T. J. Ward, who has also made cultivations of the moulds and isolated from them a species of *Aspergillus*.

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The National Physical Laboratory

ABSTRACTS OF PAPERS PUBLISHED IN 1936*

THIS pamphlet contains abstracts of the official papers, numbering 140, published from the National Physical Laboratory in the scientific and technical press during the year 1936. It is the first of a series which will be issued annually.

In the preface the Director (Professor W. L. Bragg) points out that the purpose of the Abstracts is to provide a concise summary of the completed work of the Laboratory, supplementing the information given in the Annual Reports, and it is hoped that they will prove useful to industrial firms, research organisations, and scientific workers generally. The Laboratory will welcome opportunities of assisting British industrial firms to effect the industrial application of the results of its researches.

The Abstracts cover all the branches of work on which the Laboratory is engaged, and are grouped under the following subjects:—Heat and General Physics, Sound, Optics, Photometry, Radiology, Electrical Standards and Measurements, Electrotechnics, Magnetism, Radio, Engineering, Metallurgy, Instruments, Aerodynamics, and Ship Design and Propulsion. An author-index and a subject-index are included.

New Zealand

Department of Agriculture

ANNUAL REPORT FOR 1936–1937

THE Chemistry Section, now under the direction of Mr. R. E. R. Grimmett (in succession to Mr. B. C. Aston) has continued various investigations on the deficiency diseases of livestock.

BUSH SICKNESS.—The results of the experiments on the causes of bush sickness (*cf.* ANALYST, **1937, 62, 466**) have provided evidence that a deficiency of cobalt is a principal factor. Experiments to determine the part, if any, played by traces of other elements, notably nickel, zinc and soluble iron, are being continued in the Rotorua and Atiamuri districts. Commercial supplies of limonite intended for stock consumption are analysed periodically for cobalt to ensure that they are satisfactory in this respect. Surveys of the deposits at Okaihau and Ruatangata have shown that the different seams of irregular masses vary greatly in cobalt-content, but that by selection of the ore the resultant ground product may be maintained at a level of at least 100 p.p.m. of cobalt. Material of this standard has proved efficacious throughout the "bush sick" area. Combined with equal parts of salt it makes a lick of good consistence and attractive to stock. The colouring power of the limonite helps the farmer to detect which animals are taking the lick by the staining of the hair of their faces. A number of "trace" elements are present in these limonites and may reinforce the action of the cobalt. There is little or no danger resulting from the animals consuming quantities in excess of their requirements. It appears, therefore, that the use of limonite possesses advantages over the use of a pure cobalt salt combined only with common salt. To some extent its use may be displaced by top-dressing with fertilisers containing cobalt, but salt-licks are beneficial to stock on most classes of country, and the

* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. 1938. Price 1s. net.

addition of limonite to the salt, even in districts not considered "bush sick," may be advantageous and entails very little extra labour or expense.

Samples of the deposit of soft limonite at Maketu, Bay of Plenty, have been analysed and found to contain only 1·3 and 3·6 p.p.m. of cobalt. This figure was considered too low to warrant the expense of feeding trials.

Cobalt in Foodstuffs.—The demonstration that bush sickness is connected with a deficiency of cobalt has raised the question if it is possible to prove by experiments on small animals that this element is essential in animal nutrition. In conjunction with the Research Officer in Animal Nutrition at Wallaceville, an endeavour is being made to select a diet of purified foodstuffs extremely low in cobalt. If this endeavour is successful, feeding experiments on rats will be carried out at the Veterinary Laboratory. Cobalt has been determined in a number of samples of foodstuffs, both in their original condition and after special purification. Although very low figures for cobalt have been found in some of these foodstuffs, there are still some difficulties to be surmounted before the experiments can be made with reasonable prospect of success. Some of the figures found which may be of interest are as follows (average cobalt p.p.m. dry weight): butter, 0·013; lard, 0·007; castor sugar, 0·010; cod-liver oil, 0·004; wheat-germ oil, 0·007; corn starch, 0·003; casein, 0·011; dried yeast, 0·038.

Suspected Mineral Deficiencies connected with Plant Diseases.—*Zinc deficiency* (*Chlorosis of Citrus and other Trees*).—It has recently been found by a number of investigators in the United States, Australia, and elsewhere that certain types of chlorosis, or mottling in citrus and other fruit-trees, are connected with zinc deficiency in the soils on which the trees are growing, and are curable by applications of zinc salts either in a spray or to the soil. In view of the occurrence of chlorosis in certain citrus orchards in New Zealand, an investigation is being made jointly by the Department of Scientific and Industrial Research and the Horticulture Division of the Department of Agriculture into the possibility of this chlorosis being connected with zinc deficiency. A large number of samples of chlorotic and healthy leaves have been collected and their zinc-content is being determined. Already there are indications that chlorotic leaves from Tauranga District are significantly lower in zinc than healthy leaves, but the work is still in the preliminary stages.

Samples of cocoa leaves from trees affected with "die-back," obtained from Samoa, were also analysed for zinc. No deficiency of this element was apparent, the amount of zinc ranging from 50 to 80 p.p.m. dry weight.

Zinc Poisoning of Pigs.—Work on the toxicology of zinc in connection with suspected zinc poisoning of pigs has been continued in collaboration with Wallaceville Veterinary Laboratory. Feeding trials with young pigs under controlled conditions, using pure zinc lactate, showed that growth was retarded, and a characteristic "non-specific" arthritis, together with other symptoms, was produced. Analyses disclosed exceptionally high contents of zinc in the affected joints, and in liver and kidney. No significant storage of zinc occurred in the muscles. Further experiments to determine the approximate level of zinc consumption required to produce distinct effects have been commenced.

Limestone.—Attention is again drawn to the sale of ground shells under the description "burnt-shell" or "burnt-lime." Samples analysed have usually contained only traces of burnt lime as calcium oxide or hydroxide. Evidently some heating of the shell is practised to facilitate grinding, but is quite insufficient to convert the carbonate into oxide.

Borax Treatment of Lemons.—Difficulty experienced in a lemon-curing plant, owing to the formation of sludge in a borax dipping solution contained in a new concrete bath and resulting in an objectionable white deposit on the lemons, was found to be due to chemical action between the hot borax solution and the cement. The flocculent white precipitate was found to consist of calcium borate plus some

free boric acid. On continued use of the bath and removal of the sludge, corrosion gradually ceased, but it was recommended that metal baths should be used in future installations.

MOULD ON BUTTER.—The Dairy Division of the Department has investigated complaints about the development of mould on butter after being landed in Great Britain. As the trouble was most pronounced when the butter was packed in Saranac boxes it was therefore decided that all butter packed in boxes of this type should be wrapped in Parchfoil (a wrapping material consisting of two thicknesses of parchment paper with a layer of aluminium foil between). While it is recognised that the use of Parchfoil will not prevent the development of mould on the box, it is expected to prevent it reaching the butter.

METALLIC CONTAMINATION OF BUTTER.—The principal chemical work of the Dairy Laboratory, Wallaceville (under the direction of Dr. G. M. Moir) was the determination of the metallic contamination of butter. It was found that the great majority of creamery butters contained considerably less than the maximum desirable figure of 1·5 p.p.m. of iron, but a larger proportion of samples contained more than the desirable maximum (0·2 p.p.m.) of copper.

STANDARDS INSTITUTE.—The Director of the Chemical Section was appointed to represent the Department on the Chemical Divisional Committee of the New Zealand Standards Institute. Many specifications of a more or less routine nature affecting apparatus or methods used in agricultural chemistry were considered in detail, and a number of British Standards were adopted as New Zealand Standards. In addition, several draft standards directly concerned with the analysis or composition of primary products received very careful consideration and were circulated to all interested parties. The possibility of introducing standards for meat-meals, pig-meals, and pollards to suit the requirements of the pig and poultry industries without unduly interfering with existing manufacturing practice is being explored. As a preliminary step, representative series of samples of these materials, as offered for sale on the New Zealand market, were collected and are in course of analysis.

Palestine

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1936

THE Government Analyst (Mr. G. W. Baker) reports that 9188 samples were examined, as compared with 11,194 in 1935; the decrease was mainly due to reduction in the sampling of milk and foods owing to the political disturbances.

FOOD AND DRUGS.—Of the 5556 samples of food examined, 3276 were of milk, and, of these, 6 per cent. were below standard.

Samples of cheese sold as Palestinian produce consisted of imported cheese incorporated with imported dried milk and other ingredients. As the law stands at present this procedure is apparently not illegal.

Vinegar.—Seven of 9 samples were deficient in acid or improperly labelled. Under the regulations, imitation vinegar is allowed, if labelled as such.

CONTROL OF SOAP FACTORIES.—Under the terms of the trade agreement, soap of certified quality is favoured by a lower customs duty, and Government control of approved soap factories exporting olive oil soap to Egypt has therefore been established. Sixty-two samples of soap and 114 samples of olive oil were examined during the year. This measure has been introduced with the express purpose of assisting the old-established soap-making industry of Nablus.

POLICE DEPARTMENT.—*Poisoning Cases.*—In connection with 20 cases of suspected human poisoning, fatal and otherwise, 78 specimens were examined.

In 13 of these cases poison was detected as follows:—arsenic 5, cyanide 1, lysol 1, naphthalene (moth-ball) 1, veronal and allied drugs 3, alcohol 1.

Shooting and Bombing.—Under the Emergency Regulations the definition of the term explosive has been widened to include certain substances which, though not explosive in themselves, are commonly used as ingredients in the manufacture of explosives, and in many cases of seizure the police have submitted specimens for identification. Old military bombs, both British and Turkish, have also been examined for identification of the filling. A variety of home-made bombs has included tin canisters and cast-iron pipe fittings filled with explosive material carrying a fuse and detonator. Picric acid (lyddite) and gelignite have frequently been identified. The picric acid is presumably obtained from old Turkish shells. One "bomb" examined consisted of about a pound of gelignite, carrying a detonator and fuse and was studded all over with large-headed nails.

Development of Finger-prints on Bitumen.—In one case an alarm clock had been converted into an electric time-fuse to fire a large bomb containing picric acid, and the back of the clock had been given a coat of bitumen on which finger-prints were discernible. Unfortunately these prints could not be developed by dusting with powder, as the bitumen was tacky. It was noted, however, by the finger-print officer that the prints, if breathed upon, became more visible as an effect of the condensation of moisture. A special "cold stage" was therefore made, and when the exhibit was placed on this the condensed moisture remained long enough for exposure of several minutes, and, by the use of a 3-inch objective, satisfactory photographs of the prints were obtained.

Identification of Automatic Pistol Bullets.—In one of the many shooting cases five cupro-nickel coated bullets bearing well-defined rifling marks were examined. In at least two of the land impressions and one of the grooves impressions on each bullet secondary markings were found providing conclusive evidence that all were fired from one pistol.

DEPARTMENT OF AGRICULTURE.—*Artificial Honey.*—Beekeepers have represented to the Government the necessity for curtailing the sale of adulterated honey and honey substitutes, and as a result legislation is being drafted to make illegal the use of the word "honey," or any inscription suggesting honey, in the labelling of imitation honey. At present, flavoured invert sugar and glucose syrups are being sold as "artificial honey." Assistance has also been given in drafting grading regulations for export honey.

Pan-formation in Citrus Soils.—Some observations and experiments have been carried out in connection with pan (Nazas) formation in the local red sandy soils of the citrus belt. The results are consistent with the view that the Nazas is a degradation product brought about by the removal of the binding link between the clay and sand. This link is chiefly calcium which may be removed by the living tree and the base exchange effect of rainfall and irrigation. Subsequent separation of the aluminium and iron results in the appearance of the dark nodules of iron oxide, which are the first signs of Nazas formation. Addition of lime, avoidance of excessive irrigation, and the use of humus-forming manures are protective measures.

WEIGHTS AND MEASURES.—The introduction of the metric system, which was the purpose of the Weights and Measures Ordinance of 1928, is still postponed.

All-India Institute of Hygiene and Public Health, Calcutta

ANNUAL REPORT FOR THE YEAR 1936

THE Report of the Institute, which is under the direction of Lt.-Col. A. D. Stewart, M.B., D.P.H., deals with its dual functions as a centre for advanced studies in public health and for research (*cf.* ANALYST, 1935, **60**, 615). An account is given of the work of the six sections of the Institute, and attention is directed to the results of various investigations.

MUSTARD-SEED OIL AND EPIDEMIC DROPSY.—Evidence strongly supporting the "mustard" oil theory was obtained at Jamshedpur, which has a population of about 100,000, composed of people from practically all the provinces of India, with a small number of non-Indians. There were 185 cases of epidemic dropsy in 52 Bengali families, and 37 cases in 14 non-Bengali families. The use of a particular brand of mustard-seed oil from a local oil mill, purchased within a period of 5 weeks just prior to the outbreak, was a feature common to 95·5 per cent. of the affected families, whilst there was conflicting evidence as to the remaining 4·5 per cent.

By the use of the mustard-seed oil obtained during the outbreak the signs and symptoms of epidemic dropsy have subsequently been produced in a number of persons.

BACTERIOLOGICAL INVESTIGATION OF RICE.—It was found that (1) commercial formalin is not a reliable disinfectant for sterilising the surface of certain varieties of rice grain; (2) the surface of rice grains can be effectively sterilised with a 0·1 per cent. solution of mercuric chloride acidified with 0·5 per cent. of hydrochloric acid; (3) if surface sterilisation is effective, it is not possible to demonstrate the presence of "rice bacilli" in the central or other types of opacities in the rice grain; (4) the traces of mercuric chloride left on the surface of the grain do not interfere with the growth of the organism when it is artificially introduced into the centre of the grain and the opening of the cavity is sealed.

Attempts to produce opacities artificially in clear white grain by storage under suitable conditions of temperature and humidity, after inoculation with "rice bacilli," proved unsuccessful.

Samples of rice were obtained from various districts of Madras Presidency. Some of these showed very high proportions of grains with opaque centres, but spore-bearing aerobes could not be cultivated from the opaque portions.

The Report of the Professor of Biochemistry and Nutrition (Dr. H. E. C. Wilson) is devoted mainly to the results of investigations on nutrition.

PHYSICAL AND NUTRITIONAL SURVEY.—The examination of about 4500 children in Calcutta and of 1250 in Ferozepore (Punjab) has been completed. The data obtained in Calcutta show that the poorer classes are probably suffering from a deficiency in the quantity and quality of the protein rather than from lack of a specific vitamin.

VITAMIN B_1, B_6 AND FLAVIN.—The assay of vitamin B_1 in 80 foodstuffs has been completed, and the B_6 and flavin components are now being examined. Flavin is being estimated both chemically and biologically, and the use of colorimetric and fluorescent methods is being investigated.

ABSORPTION AND METABOLISM OF CAROTENE.—The absorption of carotene on different diets has been investigated both in animals and in man. The data on animals show that carotene is better absorbed when fed in the natural state (spinach) or dissolved in oil than when given in a watery suspension. The absorption of carotene does not appear to be affected by adding bile salts or extra meat to the diet to promote a flow of bile, but the evidence obtained from an examination

of the liver showed that transformation into vitamin A may have been more efficient under those conditions. In the human subject the absorption of carotene fed as spinach was better on a fat diet than on one poor in this foodstuff. There was evidence that the active β-carotene was selectively absorbed by the intestine. The absorption of vitamin A by the human subject appears to be complete, as judged by negative results of tests on the faeces. The significance of these findings for India, where carotene is the only source of vitamin A for many, needs no stressing. The importance of fat in promoting the absorption of carotene, and possibly of meat in effecting its transformation into vitamin A, should be a guide to those interested in practical nutrition not to consider any one food or vitamin to the exclusion of the rest of the diet. Work is in progress on the mechanism and site of transformation of carotene into vitamin A in the organism.

Georgia Experiment Station

ANNUAL REPORT FOR THE YEAR 1936–37

THIS is the forty-ninth Annual Report of the Georgia Experiment Station, whose Director is Mr. H. P. Stuckey. The Station co-operates with other units of the University System of Georgia with other State agencies, and with the Federal agencies, in an effort to co-ordinate the research work of the State in relation to agriculture.

The Report includes sections on agricultural economics, agronomy, pasture investigation, animal industry, chemistry and botany. Among the subjects investigated are the following:

AVAILABILITY OF DIFFERENT FORMS OF CALCIUM PHOSPHATE AS FERTILISERS.—In tests made at 11 different points in the State the results did not show any great difference between monocalcium phosphate and dicalcium phosphate, but tricalcium phosphate did not give as good results as the other two forms.

COTTON NUTRITION.—Calcium in dried cotton leaves has been separated into four fractions, and some evidence has been obtained which indicates two other fractions. An appreciable portion of the element has been found to be present as tricalcium phosphate, while another fraction seems to be present in an exchangeable form. Each fraction from leaves of plants fertilised with nitrate was higher in calcium than the corresponding fraction from leaves of plants grown on ammonium salts. The necessity for manganese for normal growth of the cotton plant has been established. The addition of 0·1 p.p.m. of manganese to the culture solution caused a decided improvement in the growth of cotton plants in the first three weeks of the seedling stage.

MUSCADINE GRAPE STUDIES.—Carbohydrate determinations on muscadine grape cuttings, collected each month from May through November, showed that reducing sugars remained fairly constant until November, when they increased to approximately twice the previous values. Sucrose decreased slowly to a very low concentration during the fruit-ripening stage and then increased rapidly until the end of the study period. The fraction hydrolysable by acid remained rather constant throughout the period studied. Determinations of the non-volatile acids in several varieties of muscadine grapes showed that the principal acid is tartaric, and that citric and malic acids are present in traces only. Preliminary examination of the pigment of the Hunt variety of muscadine grapes indicates that the colour is due to a mixture of diglycosides of delphinidin and syringidin.

AVAILABLE IRON IN VEGETABLES.—The available iron was determined chemically by the dipyridyl method in peas, spinach, peanut meal, turnip greens, collards, head lettuce, mustard and leaf lettuce. Haemoglobin regeneration on

feeding these vegetables was highest with peas and ranked in the order given, leaf lettuce giving the least recovery. The results were not parallel, or in any way co-ordinated, with the biological assay. The factor accounting for the observed irregularities has yet to be determined.

AVAILABLE CALCIUM IN VEGETABLES.—In a preliminary survey of available calcium in turnip greens, collards, kale and spinach it was found that the calcium was exceptionally well utilised except in spinach, which gave a very low utilisation factor.

PIMIENTO IN NUTRITION.—Cows depleted of their vitamin A requirements were fed for three weeks with dried pimiento. Samples of milk taken at the end of the depletion period and at the close of the pimiento feeding were tested on rats, the Sherman technique for estimating vitamin A being used. The increase in vitamin content of the pimiento milk was three to four-fold.

VITAMINS IN PEACHES.—During the peach season of 1936 vitamin estimations were made on Elberta and Hales peaches. It was shown that in both varieties 1 unit of vitamin A was present in about 80 mg., and in Elberta peaches 1 unit of vitamin B (B_1) was present in about 5 g. and 1 unit of vitamin G (B_2) was present in about 3 g.

British Standards Institution

APPARATUS FOR THE DETERMINATION OF SMALL QUANTITIES OF WATER BY DISTILLATION WITH AN IMMISCIBLE LIQUID

B.S.I. SPECIFICATION, NO. 756—1937*

When accurate and reproducible results are required in the determination of small amounts of water by entrainment distillation, a completely standardised apparatus is desirable, and the present specification has been prepared to meet this need. The specification is based on the apparatus described by Tate and Warren (ANALYST, 1936, **61**, 367). To obtain the best results it is necessary to adhere to the procedure and choice of immiscible liquids prescribed in that paper.

This Specification requires reference to B.S.I. Specification, No. 572.—Interchangeable Conical Ground Glass Joints.

BRITISH STANDARD METHODS FOR TESTING GELATINS

B.S.I. SPECIFICATION, NO. 757—1937†

The tests described fall under two heads: (1) Physical tests which are mainly determined by the degree of hydrolysis; (2) Chemical tests which concern freedom from associated substances.

In Part I of the Specification directions are given for the preparation of the sample, the concentrations and the method of solution.

Part II comprises:—(A) Determination of moisture-content. (B) Determination of jelly strength. (C) Determination of jelly strength by the Bloom gelometer (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 348). (D) Determination of viscosity. (E) Determination of melting-point. (F) Determination of foam. (G) Determination of water absorption. (H) Determination of the Solubility of partially swollen sheet. (J) Determination of keeping quality. (K) Determination of *p*H. (L) Determination of grease. (M) Determination of ash. (N) Determination of sulphur dioxide. (O) Determination of chlorides. (P) Colour of jelly and of solution. (Q) Determination of clarity. (R) Determination of arsenic (by the Gutzeit method). (S) Determination of heavy metals.

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* Copies may be obtained from the Publications Department, British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2s. net; post free 2s. 2d.

† Copies may be obtained from the Publications Department, British Standards Institution, 28, Victoria Street, London, S.W.1. Price 3s. 6d. net; post free 3s. 8d.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Isolation of Glutathione from Wheat Germ. B. Sullivan and M. Howe. (*J. Amer. Chem. Soc.*, 1937, **59**, 2742–2743.)—Glutathione has been found to be the cause of the deleterious action of wheat germ on the baking quality of the flour. To isolate the substance 2 kg. of fresh wheat germ are treated with 5 litres of hot water and 50 g. of sulphosalicylic acid followed by filtering, centrifuging and treatment of the supernatant liquid with neutral lead acetate. The lead precipitate is ground with 0·5 *N* sulphuric acid, centrifuged and filtered, and the copper, mercury, and silver salts are precipitated successively in the usual way. The final silver salt precipitate is treated with hydrogen sulphide and filtered off, absolute ethanol is added to the filtrate, and the solution is rapidly evaporated to dryness in a vacuum desiccator over phosphorus pentoxide. The best means of removing traces of ash from the glutathione is by successive silver salt precipitations. Glutathione thus obtained melted at 189–190° C., with previous softening at 147° C. Yields of 0·1–0·2 g. were obtained from 2 kg. of wheat germs.

D. G. H.

Further Observations on the Component Glycerides of Olive and Tea-seed Oils. T. P. Hilditch and H. M. Thompson. (*J. Soc. Chem. Ind.*, 1937, **56**, 434T–438T.)—Palestine olive oil from the same source as that used by Thorbjarnarson and Drummond (ANALYST, 1935, **60**, 23) resembles the majority of olive oils from other sources in containing the following component fatty acids in percentages by weight:—palmitic 10·7, stearic 3·6, arachidic 0·1, oleic 76·4, linolic 9·2. Previous work (Hilditch and Jones, *J. Soc. Chem. Ind.*, 1934, **53**, 13T; Abst., ANALYST, 1934, **59**, 194) has shown that, whilst in cotton-seed, linseed and soya-bean oils tri-C_{18}-glycerides are present in quantities which are close to the minimum amount consistent with the composition of the respective total fatty acids of each oil, the corresponding results for olive and tea-seed oils are about 10 per cent. less than the minimum amount consistent with the fatty acid analyses. This anomaly is subjected to further inquiry. To eliminate the influence of small amounts of volatile substances naturally present in vegetable oils or formed during slight rancidification, a very small initial fraction of the methyl esters of the liquid fatty acids was collected, and the lower fatty acids were then sought for in the subsequent fractions. In addition, the method of Longenecker (*J. Soc. Chem. Ind.*, 1937, **56**, 199T; Abst., ANALYST, 1937, **62**, 696) for the separation and determination of small proportions of hexadecenoic acid and similar lower unsaturated acids by the use of an electrically heated fractionating column was employed. It was found that hexadecenoic acid occurs in olive and tea-seed oils in amounts not exceeding 1 per cent. of the total fatty acids, and this was confirmed by hydrogenation of the esters of the liquid fatty acids before fractionation. This amount of hexadecenoic acid is not sufficient to explain the discrepancy mentioned. By a method depending upon a study of the oils after progressive hydrogenation

to several stages it was found that the tri-C_{18}-glyceride contents of Tuscany and Palestine olive oils are in good agreement, and that of tea-seed oil in fair agreement, with the minimum amounts of these glycerides consistent with the fatty acid compositions of the oils, especially if allowance is made for the presence of 1 per cent. of hexadecenoic acid. In the estimation of tristearin by fractional crystallisation of the completely hydrogenated oils from ether (Hilditch and Jones, *loc. cit.*) it was concluded that the procedure is not reliable when the content of tristearin in the mixture of completely saturated triglycerides lies between 50 and 70 per cent., and that this failure of the method is the cause of the anomalous results in the previous work. The method is satisfactory when the tristearin-content is above 75 per cent. or below 40 per cent. of the saturated triglycerides. A. O. J.

Papaya Seed Oil. H. W. von Loesecke and A. J. Nolte. (*J. Amer. Chem. Soc.*, 1937, **59**, 2565–2567.)—The papaya tree, *Carica papaya*, which grows in most tropical countries, produces melon-like fruits varying in diameter from 4 to 20 inches, and weighing up to 4½ lb. The skin is smooth, the flesh is yellow to deep salmon-pink, and each fruit contains about 1500 round black wrinkled seeds with gelatinous membranes. The seeds, each of which weighs about 0·09 g., constitute about 7 per cent. of the weight of the fruit and contain 85 per cent. of moisture. A sample of air-dried seed contained: moisture, 7·47; ash (soluble), 3·83; (insoluble), 4·02; protein, 27·20; fat, 25·29 per cent. The oil was a yellowish-brown liquid with a cress-like odour and taste, and had the following characteristics:—sp.gr. at 20/20° C., 0·9091; n_D^{20}, 1·4666; saponification value, 189·5; iodine value (Hanus), 72·6; acid value, 3·05; unsaponifiable matter, 1·32 per cent.; Reichert–Meissl value, 1·05; Polenske value, 0·20; acetyl value, 3·8; Hehner value (corr. for unsaponifiable matter), 95·9; saturated acids (corr.), 16·94; unsaturated acid (corr.), 78·63 per cent. The fatty acids had the following composition:—palmitic, 11·94; stearic, 5·49; arachidic, 0·32; oleic, 79·94; linolic, 2·22 per cent. A volatile oil (to which the cress-like odour is due) was also present (0·09 per cent. by wt. on the seed). D. G. H.

Some Constituents of the Cannonball Fruit. E. K. Nelson and D. H. Wheeler. (*J. Amer. Chem. Soc.*, 1937, **59**, 2499–2500.)—The cannonball tree, *Couroupita guianensis* Aubl., is a tropical tree of the humid forests of South America, and has been described on several occasions (*e.g.* Dahlgren, Field Museum of Natural History, Botany Leaflet No. 6, 1924). The fruits, 6–8 in. in diameter, are round and have hard shells entirely filled with pulp. The pulp (1739 g. from one fruit) contained a small amount of volatile oil with the peculiar odour of the fruit and the constituents of which included a phenolic substance and acids. A red colouring matter obtained from the pulp was evidently a carotenoid pigment. The pulp juice was neutralised and the acids were recovered from the lead precipitate and esterified. The esters were treated with ether, washed, separated and distilled. The fraction boiling at 172–174° C. (the greater part of the distillate) was re-fractionated, and citric trihydrazide was isolated. The lower-boiling fraction yielded malic hydrazide, whilst the residue from the main fraction in the flask, on re-distillation through a Vigreux column, yielded iso-citric trihydrazide.

The cannonball fruit appears to be the second in which iso-citric acid has been identified, although it is not in this fruit the predominating acid, as in the blackberry. D. G. H.

Sardine-liver Oil. Y. Toyama. (*J. Soc. Chem. Ind., Japan*, 1937, **40**, 402B–403B.)—The oils were extracted from the livers of sardines, *Sardinia melanosticta* (Temninck and Schlegel), obtained in 4 different catches, the livers being preserved in alcohol for about 10 days to 2 months between removal from the fish and the extraction. The livers from the first catch were extracted with about 2 litres of ether, the ethereal solution was washed with water and dried, and the ether was removed by distillation; the oil was taken up in petroleum spirit, and the solvent was distilled from the filtered solution. For samples 2, 3 and 4, the livers were extracted with about 3 to 5 litres of petroleum spirit, the solution was washed with 50 per cent. alcohol, and the solvent was distilled. The extraction of oil did not appear to be complete, and some oil was lost by the formation of an emulsion during the washing of the solution. The oils were dark orange-yellow, and appeared to contain phosphatides; their characteristics are shown in the following table:

	No. of sample			
	1	2	3	4
Sp.gr. at 20° C./4° C.	0·9335	0·9347	0·9229	0·9272
n_D^{20}	1·4829	1·4838	1·4815	1·4817
Acid value	9·35	7·45	14·8	6·67
Saponification value	186·2	181·2	177·0	178·1
Iodine value (Wijs)	185·3	186·1	192·9	194·8
Unsaponifiable matter, per cent.	3·44	5·35	5·15	5·28
Cholesterol in unsaponifiable matter, per cent. (determined by the digitonide method)	—	49·17	45·88	57·20
Ether-insoluble bromides of fatty acids, per cent.	60·82	66·41	68·60	66·16
"Cod-liver oil value" (determined with Lovibond tintometer)	3·7	9·0	6·2	7·0
Reaction with sulphuric acid	Violet colour contaminated with a brown hue.			
Reaction with antimony trichloride in chloroform	Blue colour rapidly becoming brown, especially with high concentrations of oil.			

The iodine values of these oils are a little higher than those of sardine oils. The unsaponifiable matter is a mixture of crystals and liquid at the ordinary temperature; re-crystallisation from alcohol yields pure cholesterol. A sample of sardine-liver oil examined by Kawakami (*Bull. Inst. Phys. Chem. Research*, 1932, **11**, 968) had a "cod-liver oil value" of 100; further work is needed to explain such great variations in the "cod-liver oil values" of fish-liver oils. E. M. P.

Composition of the Liver Fats of some New Zealand Farm Animals. T. P. Hilditch and F. B. Shorland. (*Biochem. J.*, 1937, **31**, 1499–1515.)—The composition of the component fatty acids present as glycerides and phosphatides respectively in the livers of New Zealand oxen, cows, sheep and pigs, has been investigated, and compared with available data for the corresponding depot fats. The usual method of phosphatide-glyceride separation (Hilditch, *Biochem. J.*, 1934, **28**, 779) was found to be incomplete, owing to the slight solubility in acetone of

di- and tri-saturated glycerides typically present in animal fats, and a third intermediate fraction has been used. The phosphatide data for the component acids of cow-, pig-, and sheep-liver fats are regarded as accurate almost to the usual limits of the ester fractionation method (except for the highly unsaturated C_{20} and C_{22} acids from which pitch-black residues are obtained). The data for the glyceride fraction may not be so reliable, owing to the presence of free fatty acids and, to a minor extent, of cholesteryl esters of uncertain composition. The main error involved was to increase the apparent acid in the phosphatide fraction at the expense of the glyceride fraction, but the error for the individual fatty acid was usually small. The uncorrected palmitic acid content of cow-liver glyceride, however, is 29·8 per cent. (mol.) and the corrected figure 34·7 per cent. (mol.). The non-phosphatide fatty acids of the liver bear some resemblance to the corresponding depot fats, but contain higher proportions of hexadecenoic acid, 5 to 10 per cent. (mol.), and of C_{20}–C_{22} highly unsaturated acids, 5 to 15 per cent. (mol.). The presence of hexadecenoic acid (3 to 4 per cent., mol.) in the depot fats, not before reported, together with the relatively constant 25 to 30 per cent. (mol.), of palmitic acid in the liver "glyceride," emphasise the resemblance. The liver phosphatides contain more stearic, C_{20}, and C_{22} unsaturated acids, and less hexadecenoic acid than the corresponding liver "glyceride," and have a marked tendency to contain acids of higher molecular weights. Cow- and ox-liver fatty acids contained no linolic acid in detectable proportions, but traces were found in pig- and sheep-liver fatty acids. Linolenic acid was present in sheep-liver fatty acids. D. G. H.

Further Study of the Component Acids of Ox Depot Fat with Special Reference to Certain Minor Constituents. T. P. Hilditch and H. E. Longenecker. (*Biochem. J.*, 1937, **31**, 1805–1819.)—Three beef tallows have been examined in detail. The major components were: oleic, 38 to 40; palmitic, 26·5 to 31; stearic acid, 20·1 to 25·4 per cent. The composition was that usually found in land animal depot fats, which contain relatively constant amounts of palmitic acid (25 to 30 mol. per cent.) and total C_{18} acids 65 to 70 mol. per cent. Among the minor constituent acids were myristoleic ($\Delta^{9:10}$-tetradecenoic) 0·5 per cent.), and palmitoleic ($\Delta^{9:10}$-hexadecenoic) 2·0 to 2·8 per cent. Tetradecenoic acid has not previously been reported in a land animal depot fat, although present in several aquatic animal depot fats, whilst hexadecenoic acid, also a usual component of fish oils, has been recognised in a few depot fats of higher types of land animals. The occurrence of the two acids in the ox-fats in less amounts than in the fats of amphibians or reptiles seems to follow the general trend of simplification of the mixed fatty acids running parallel with the scale of evolutionary development. The constitution of the C_{18} unsaturated acids shows them to be a mixture, chiefly of oleic acid ($\Delta^{9:10}$-octadecenoic) and a small amount of geometrically isomeric linolic acid ($\Delta^{9:10,\ 12:13}$-octadecadienoic acid). Arachidic acid is calculated as 0·3 to 1·0 per cent. mol., myristic 2·3–3·7, and octadecenoic 1·7 to 1·8 per cent. mol., whilst arachidonic and lauric acids may be present in very small amounts—0·1 to 0·5 and 0·2 per cent. (mol.) respectively. Previous analyses of ox and sheep depot fats are reviewed in the light of the present work, and the increase in fully-saturated glyceride content of these fats with increasing stearic acid content is confirmed. D. G. H.

Component Fatty Acids of the Phosphatides of Soya-bean and Rape Seeds. T. P. Hilditch and W. H. Pedelty. (*Biochem. J.*, 1937, **31**, 1964–1972).—Samples of the alcohol-insoluble ("kephalin") and alcohol-soluble ("lecithin") phosphatides of soya bean and of the alcohol-insoluble phosphatides of rape seed were hydrolysed first with sulphuric acid and then with potassium hydroxide. The fatty acids so obtained were identified by established methods. The composition in mol. per cent. of the phosphatides, together with those of the corresponding glycerides, was as follows:

	Soya bean			Rape seed	
	Glycerides	Phosphatides		Glycerides	Phosphatides
Fatty acid		Alcohol insoluble	Alcohol soluble		Alcohol insoluble
Myristic	1	—	—	—	1
Palmitic	8	13	19	2	9
Stearic	5	4	—	—	—
Arachidic ..	Trace	1	—	—	—
As Behenic ..	—	—	—	1	1
Hexadecenoic ..	—	10	6	—	2
Oleic	26	10	18	19	23
Linolic	54	53	52	31	44
Linolenic ..	6	4	4	—	—
As C_{20} unsaturated	—	5	1	—	—
Erucic	—	—	—	47	20

It is significant that in both seeds all the characteristic fatty acids of the glycerides are found in the phosphatides. Linolic acid appears to be the most important component of plant phosphatide acids. F. A. R.

New Alkaloids in *Aconitum napellus*. W. Freudenberg and E. E. Rogers. (*J. Amer. Chem. Soc.*, 1937, **59**, 2572–2575.)—The mixture of residual bases obtained in the commercial preparation of crystalline aconitine from tubers of *Aconitum napellus*, which is the so-called amorphous aconitine, was treated essentially by the method of Schulze (*Arch. Pharm.*, 1924, **262**, 553). Fractionation of the ether-soluble alkaloids contained in the base yielded two new alkaloids, called "napelline" and "neoline." The fraction 1*b* (corresponding with Schulze's neopelline) was further fractionated by dissolving it in the minimum amount of 0·1 *N* acid, and adding the equivalent of 0·1 *N* sodium hydroxide solution; the precipitate was filtered off and neutralised with dilute hydrobromic acid, and the resulting hydrobromide was crystallised from a mixture of methyl alcohol and ether. The napelline base had the composition $C_{22}H_{33}NO_3$. The filtrate from the napelline preparation was extracted with ether and yielded a base which was isolated as the crystalline hydrobromide; from its physical properties and elementary composition it appears to be identical with Schulze's neolic hydrobromide, the formula of the base, however, being $C_{24}H_{41}NO_6$. *l*-Ephedrine and sparteine were identified in the original filtrate from the preparation of fraction 1*b*, but were present only as traces. The identified bases, including the two new ones, account for approximately 60 per cent. of the entire mixture of residual bases. D. G. H.

Stability of Tannin Solutions (for Burns). P. Van der Wielen. (*Pharm. Weekblad*, 1937, **74**, 1589–1590.)—Solutions of tannin may be used in the treatment of burns to protect them from infection by external contamination. According to E. Davidson of the Henry Ford Hospital, Detroit, no bandage is required, and if no tannin is available, strong tea may conveniently be used; the origin of the latter expedient is attributed to the Chinese. A fresh 5 to 10 per cent. solution of tannin in warm water should be prepared for this purpose, but on storage this deteriorates, owing to the growth of moulds and bacteria and to oxidation, which results in the darkening of the solution and the formation of dark-coloured flocks. The former trouble is avoided by sterilisation, and the latter (which is accelerated by alkali from the glass containing-vessel) by the presence of carbon dioxide (*cf.* Woodard and Cowland, ANALYST, 1933, **58**, 553). J. G.

Biochemical

Digestion of Reconstituted Cream. G. A. Hartwell. (*J. Soc. Chem. Ind.*, 1937, **56**, 442T–444T.)—Reconstituted creams made in a well-known type of machine were treated with water and the commercial pancreatic substance used by Clifford (*Biochem. J.*, 1934, **28**, 418) at 38 to 39° C., and the rate of digestion was compared with that of dairy creams under the same conditions. A typical experimental mixture consisted of 80 ml. of cream, 280 ml. of distilled water and 40 ml. of a 2 to 4 per cent. solution (according to its specific activity) of the pancreatic substance. The ingredients were mixed while cold, the pancreatic substance being added last, and, after the mixture had been shaken, a 20-ml. portion was removed, diluted with about 150-ml. of boiling water, and titrated with 0·1 *N* sodium hydroxide solution, phenolphthalein being used as indicator. The remaining portions of the samples under investigation were maintained at 38 to 39° C. in a large water-bath, and 20-ml. portions were withdrawn for titration at suitable intervals. Control experiments were made with a boiled solution of the pancreatic substance. Three samples of dairy cream were used, in which amount of fat (determined by the Babcock process) varied from 48 to 52 per cent. Two kinds of reconstituted cream were used, one (containing about 33 per cent. of fat) made according to directions supplied with the machine and the other (containing about 42 per cent. of fat) made according to a recipe frequently used in cooking, *viz.* 1 lb. of butter to 1 pint of milk. The amount of dairy cream used was so adjusted that each digestion mixture contained about the same amount of fat, the total volume being maintained by the addition of more water. In all experiments the reconstituted cream was digested more rapidly than the dairy creams. Even when the volume of cream used was kept constant and the percentage of fat in the reconstituted cream was lower than that in the dairy cream, the former produced more fatty acid per cent. in unit time. There was some variation in the rate of digestion of the dairy creams, one sample being invariably digested more rapidly than the other two. The rate of digestion of reconstituted cream was not affected when different butters were used, and cream made from salt butter was digested at the same rate as that made from fresh butter, this being in accordance with the

observation of Clifford (*loc. cit.*) that sodium chloride has no effect upon lipase action. The use of a higher temperature in preparing reconstituted cream results in a more rapidly digested product, and microscopical examination showed that, in these samples, the fat is more completely emulsified. Neither pasteurisation nor storage in a refrigerator over-night appears to affect the rate of digestion. Experiments made with different proportions of butter showed that, with digestion mixtures of equal fat-content, the fat was more completely digested at the lower concentration. The fat-globules of reconstituted cream are slightly smaller than those of dairy cream. A. O. J.

Hydrolysis of Glycerides by Crude Pancreas Lipase. A. K. Balls, M. B. Matlack and I. W. Tucker. (*J. Biol. Chem.*, 1937, **122**, 125–137.)—The hydrolysis of tristearin with pancreatic lipase has been carried out to practical completion. The velocity of the reaction is at first high, but attains a steady value in a short time. The fat remaining after partial hydrolysis consists almost entirely of tristearin, so that the composition of the substrate remains almost unchanged throughout the hydrolysis. The hydrolysis of monostearin is approximately unimolecular, and the velocity of the reaction is higher than that of tristearin.

The effect of temperature on the hydrolysis of the triglycerides is very marked with those containing C_8 or higher acids and is greater the higher the fatty acids. At 0° C. the velocity of hydrolysis increases with the carbon-content of the fatty acid up to C_7, then abruptly decreases; with the higher fatty acids the velocity is practically nil. Glycerides of fatty acids lower than C_8 are split little, if any, faster at 40° C. than at 20° C. At 40° C. the glycerides with fatty acids from C_8 to C_{14} hydrolyse at approximately the same rate. In general, glycerides containing the C_7 to C_{10} acids undergo hydrolysis most easily. This does not apply to unsaturated glycerides, for olein behaves as though it contained a C_9 rather than a C_{18} acid. F. A. R.

Hydrolytic Properties of *Carica papaya* Latex and Latex Preparations. M. Frankel, R. Maimin and B. Shapiro. (*Biochem. J.*, 1937, **31**, 1926–1933.)—On the basis of experiments with commercial preparations, Willstätter defined papain as an enzyme which splits proteins but does not attack peptones, except on activation, *e.g.* by the addition of hydrogen cyanide or hydrogen sulphide. Latex, however, obtained from the fruits of *Carica papaya* grown under natural conditions, splits both gelatin and peptone, even without previous treatment with hydrogen cyanide. On keeping, the activity towards gelatin increased and the activity towards peptone decreased, but never fell to zero. Ether-treated latex showed a higher activity towards peptone and gelatin than the untreated latex. When this ether-treated latex was centrifuged, the enzymic properties of the natural latex were exhibited by the supernatant fluid. On treating this with alcohol, a precipitate was obtained that was fully active towards gelatin, but less active towards peptone than the original aqueous solution. The residue from the centrifuge, on the other hand, possessed the properties commonly attributed to papain, acting on gelatin directly, but on peptone only after activation with hydrogen cyanide. No natural hydrolytic activator could be detected in the fruit pulp press juice, but the presence, in the aqueous fraction of the latex, of a

thermostable activator of peptone cleavage was demonstrated. Since this fraction did not activate gelatin cleavage, the mechanism of activation is clearly different in the two preparations. F. A. R.

Provitamin D of Plants. A. Windaus and F. Bock. (*Z. physiol. Chem.*, 1937, **250**, 258–261.)—It has been assumed that the provitamin D of animal sterols is 7-dehydrocholesterol, that the provitamin of the sterols of higher plants is 7-dehydrositosterol or 7-dehydrostigmasterol, and that the provitamin of the sterols of fungi is ergosterol. There is considerable doubt concerning the identity of the provitamin D of plant sterols, since the provitamin-content is, in general, too low to render identification possible:

Material	Sterol in air-dried material Per Cent.	Provitamin in phytosterol Per Cent.
White cabbage	0·011	0·05
Spinach	0·011	1·02
Beans	0·015	0·10
Horse-chestnuts	0·012	0·76
Swedish turnip	0·004	0·28
Carrots	0·004	0·17
Scopolia root	—	1·40
Wheat germ	—	1·23
Cotton-seed oil	—	5·0

The provitamin D of cotton-seed oil has now been isolated in almost pure form by chromatographic analysis. It was converted into a number of derivatives, and its identity with ergosterol was thereby established. Its antirachitic activity after irradiation confirmed this, since irradiated 7-dehydrositosterol is almost inactive. The provitamin D of scopolia root could not be isolated by chromatography. The richest fraction obtained in this way contained only 5 per cent., but on exposing an alcoholic solution of this fraction to light in presence of eosin, ergopinacone was isolated and identified. Thus ergosterol is the provitamin D in the sterols of both cotton-seed oil and scopolia root. F. A. R.

Colour Reactions of Sex Hormones. K. Voss. (*Z. physiol. Chem.*, 1937, **250**, 218–220.)—Several of the sex hormones give characteristic colours with 1-nitroso-2-naphthol and nitric acid. About 1 mg. of substance is dissolved in 3 drops of warm alcohol, and the solution is diluted with 10 ml. of water, giving an opalescent suspension. One ml. of this suspension is transferred to a test-tube and treated with 1–2 drops of a 0·1 per cent. alcoholic nitrosonaphthol solution and 5 drops of strong nitric acid (sp.gr. 1·4). The test-tube is then placed in a beaker of boiling water. Androsterone and progesterone give no colour, oestrin gives a deep red, equilin a bluish-red, and equilenin a bluish-violet colour. The red colour given by oestrin is unchanged on further heating, but the colour due to equilin changes first to bluish-violet, then to green, and finally to yellow, and that of equilenin to green and then to yellow. These colour reactions are in accordance with the observation that with nitrosonaphthols phenols give red colours, naphthols violet to blue, and anthrols green. The colour changes that occur when equilin and equilenin are further heated are due to oxidation from the

naphthol (blue) to the phenanthrol (green) followed by complete destruction (yellow). In the absence of other *p*-substituted phenols, the reaction can be made quantitative by using standard solutions. A positive reaction is given at a dilution of $1:10^5$. F. A. R.

Chemistry of Vitamin E. Tocopherols from Various Sources. O. H. Emerson, G. A. Emerson, A. Mohammad, and H. M. Evans. (*J. Biol. Chem.*, 1937, **122**, 99–107.)—α-Tocopherol has been isolated as the allophanate (m.p. 158–160° C.) from cotton-seed oil, lettuce leaves, and palm oil. It is identical with the α-tocopherol previously isolated from wheat-germ oil. It has the formula $C_{29}H_{50}O_2$, and in iso-octane gives an absorption band with a maximum at 298*mμ*, for which $E^{1\%}_{1cm.} = 73$. Its *p*-nitrophenylurethane melts at 133° C. The compounds isolated from all four sources have approximately the same vitamin E activity.

β-Tocopherol was obtained from wheat-germ oil as the allophanate (m.p. 144–146° C.; $[\alpha]_D^{25} = +5{\cdot}7°$). The alcohol from this allophanate was very similar in its chemical properties and absorption spectrum to α-tocopherol, but its biological activity was distinctly less.

γ-Tocopherol was isolated from cotton-seed oil as the allophanate (m.p. 138–140° C.; $[\alpha]_D^{20} = +3{\cdot}4°$). The free alcohol had a lower biological activity than α-tocopherol. An impure tocopherol, apparently identical with γ-tocopherol, was obtained from palm oil.

It is not yet certain whether the three tocopherols are isomeric, or whether β- and γ-tocopherol contain one CH_3 group less than α-tocopherol. F. A. R.

Chemical Measurement of Vitamin B_1 in Foodstuffs and Biological Material by means of the Thiochrome Reaction. M. A. Pyke. (*Biochem. J.*, 1937, **31**, 1958–1963.)—The method of Jansen (*Rec. Trav. chim. Pays-Bas*, 1936, **55**, 1046) for the measurement of vitamin B_1 by conversion into thiochrome and subsequent measurement of its fluorescence by means of a photo-electric cell has been applied to foodstuffs and biological material containing relatively small amounts of the vitamin. When the material to be examined was a solid, *e.g.* wheat germ or ham, an extract was prepared by boiling the finely-ground or minced material with 1 per cent. hydrochloric acid; a liquid such as milk was treated directly. Four 3-ml. aliquot portions of the liquid or filtered extract were added to a mixture of 2 ml. of methanol, 1 ml. of 30 per cent. sodium hydroxide solution, and 0, 0·8, 1·0, and 1·2 ml. of 1 per cent. potassium ferricyanide solution respectively. The solutions were well mixed, then shaken with 13 ml. of isobutyl alcohol, and centrifuged. Ten ml. of the isobutyl alcohol layers were transferred to tubes, and the fluorescence was measured in Cohen's fluorometer (*Rec. Trav. chim. Pays-Bas*, 1935, **54**, 133). The deflection corresponding with the solution containing no added ferricyanide was subtracted from each of the deflections corresponding with the other solutions, and the results were each multiplied by 100 and divided by the deflection given by 10 ml. of a standard solution of quinine sulphate (0·81 mg. in 100 ml. of *N*/10 sulphuric acid). The three results should agree closely; otherwise a different range of ferricyanide should be tried until maximum fluorescence is obtained. The deflection given by the quinine solution must always be determined, in order to compensate for variations in the intensity

of the fluorometer lamp. The instrument was calibrated by means of the International Standard adsorbate. Ten mg. of this material were added to a mixture of 0·1 ml. of 1 per cent. potassium ferricyanide solution, 2 ml. of methanol and 1 ml. of 30 per cent. sodium hydroxide solution. The mixture was shaken for a few moments and made up to 5 ml. with water, then shaken vigorously with 13 ml. of isobutyl alcohol, and centrifuged. The deflection given by 10 ml. of the isobutyl alcohol extract was measured, and the reading given by a blank determination subtracted from it. The difference was multiplied by 100 and divided by the deflection corresponding with the standard solution of quinine sulphate. In this way the vitamin B_1 content of an unknown preparation can be calculated in terms of the International Standard.

The vitamin B_1 contents of various substances, as determined by fluorometric assay and by bio-assay, were found to be:

	Fluorometric assay	Bio-assay
Milk (early summer)	0·25	0·23 I.U. per ml.
Milk, raw (late summer)	0·06–0·11	— ,, ,,
Milk, pasteurised (late summer) ..	0·11–0·18	— ,, ,,
Milk, sterilised (late summer) ..	0·04	— ,, ,,
Ham	2·4	2·2 I.U. per g.
Wheat germ	10·7	6–20 ,, ,,
Dried brewer's yeast	13	6–23 ,, ,,
Egg white	Nil	Trace
Egg yolk	1·6	1·4 ,, ,,
Rice bran	5·4	5·6–7·4 ,, ,,

When pure vitamin B_1 was added to milk, ham or wheat germ 100–103 per cent. recovery was obtained in the fluorometric assay.

The amount of vitamin B_1 in urine was estimated by the same technique as that used for the International Standard adsorbate. The urine (100 ml.) was brought to *p*H 4·5 with hydrochloric acid and treated with 1 g. of fuller's earth, and 20-mg. portions of the dried adsorbate were assayed as described above. A bio-assay was not carried out on this adsorbate, but vitamin B_1 added to the urine in a second test was completely recovered. F. A. R.

Bacteriological

New Type of Beer Disease Bacterium (*Achromobacter anaerobium* Sp. nov.) producing Alcoholic Fermentation of Glucose. J. M. Shimwell. (*J. Inst. Brewing*, 1937, **43**, pp. 507–509.)—A species of bacteria recently encountered in beer by the author is described. It is Gram-negative, and therefore, as shown in a previous communication (*J. Inst. Brewing*, 1937, **43**, 111; Abst., ANALYST 1937, **62**, 232), not inhibited in growth by hop antiseptic; it is, moreover, very acid tolerant and, being anaerobic, its growth is not inhibited by exclusion of air. On these three grounds it constitutes a very serious bacterial danger to the brewer. The distinguishing characters of the organism are as follows:—*Morphology.*—Plump rods with rounded ends, diameter 1 to 1·5μ, length 2 to 3μ, but in older cultures may reach 10μ. *Arrangement.*—Single rods or pairs, in older cultures

rosette-like clusters. *Motility.*—Actively motile in young cultures. *Capsules.*—Not detected. *Spores.*—Not detected, motile cells in broth were killed in 60 minutes at 80° C. *Cultural characteristics.*—Grows in 1 per cent. glucose beer agar in an atmosphere of carbon dioxide; no growth aerobically on glucose beer agar slopes, but creamy white non-adherent growth when incubated in carbon dioxide; no liquefaction of gelatin in 6 weeks; no growth in yeast extract *sugar-free* broth, but with addition of 2 per cent. of glucose (in sealed bottles) the broth becomes densely turbid in 18–24 hours, with evolution of large quantities of gas. If incubated in glucose broth aerobically, growth begins at a depth of 3 inches or more, and eventually the carbon dioxide evolved produces anaerobic conditions and growth extends throughout the medium. The presence of a fermentable sugar is essential. *Sugars fermented.*—Glucose and fructose, with production of carbon dioxide and alcohol; maltose, sucrose and lactose not attacked. Unpleasant "stench" produced, partly due to hydrogen sulphide derived from basic medium. *Acetyl methyl carbinol.*—Not detected. *Ethyl alcohol.*—Not attacked. *Indole.*—Not detected. *Nitrates.*—Not reduced. *Optimum temperature.*—30° C. *Thermal death point.*—60° C. for 5 minutes. *Reaction tolerance.*—*p*H = 3·4 to 7·5. *Classification.*—Allocation of the species to any existing genus of the American classification is difficult. As a non-sporing anaerobe it should be classed with the *Bacterioides*, but if its anaerobic properties are disregarded, it might be classed in genus *Achromobacter.* In view of the growing tendency to avoid a sharp distinction between aerobic and anaerobic species, the organism has been classed in the latter genus and given the name *Achromobacter anaerobium.* D. R. W.

Serum Diagnosis of Enteric Fever. Report and Recommendations. A. Felix and A. D. Gardner. [*Bull. Health Organisation* (*League of Nations*), 1937, **5** [6], 223–35); *Bull. Hyg.*, 1937, 801.]—This paper deals with recommendations based upon the results of titrations in four European laboratories of the serum from about sixty-two cases of typhoid and paratyphoid fever, both by the methods ordinarily employed in those laboratories and by the standard method of the Oxford Standards Laboratory. Killed bacterial suspensions proved more reliable than living ones. The use of standardised suspensions is advised; when a dried standard serum is not available, the suspension may be compared with the Oxford standards. The following points are insisted upon:—(1) Tubes should be incubated at 50 to 52° C. in a covered water-bath, not more than one-third of the tube being submerged; (2) H agglutination should be read after 2 hours' incubation and within 10 minutes of removal from the bath; O agglutination after 20 to 24 hours' incubation and within 1 hour of removal. The reading should be made with the naked eye by oblique artificial light and against a dark background. (3) Uniformity of the end-point may be ensured by comparison with a standard tube, such as that supplied by the Oxford Standards Laboratory. (4) The density of the suspension should be 270 to 400 million organisms per ml. Sera containing lysed blood may give a fictitious agglutination at 50 to 52° C.; they should be incubated at 37° C., and the result reported with reserve. Details for the preparation of the bacterial suspensions are given. Strains are best maintained on agar stabs or Dorset's egg medium. These are plated out; for H suspensions smooth colonies

are selected, sown in broth and on agar slopes, and the suspensions are tested for agglutinability. If satisfactory, the corresponding slope is used to inoculate a large flask of broth. After 24 hours' incubation at 37° C. 0·2 per cent. of formalin is added, the flask is shaken occasionally and, after three days, tested for sterility and diluted to the required opacity. As an alternative emulsions in normal saline may be made from growths on agar slopes. For O suspensions, subcultures made from colonies are first tested for O agglutination; if satisfactory, they are suspended in normal saline, 4 volumes of 96 per cent. alcohol are added, and the suspension is kept at room temperature for 48 hours with occasional shaking. It is then centrifuged, the deposit is washed with saline, re-suspended with buffered normal saline containing 0·2 per cent. of formalin, and adjusted to the required opacity. D. R. W.

Agricultural

Value of Grass Extract and of Dried Extracted Grass in the Winter Rations of the Dairy Cow, with Special Reference to their Effects on the Carotene-Content of the Milk. F. E. Moon, J. H. Faulder and B. Thomas. (*J. Soc. Chem. Ind.*, 1937, **56**, 468–471T.)—Feeding experiments were made with 16 Shorthorn cows in order to determine the value of grass extract and of dried extracted grass in the winter ration, the effects of these foods on the carotene-content of the milk being also examined. The former was fed as a supplementary food at the rate of 4 ozs. per head per day, and the latter was used to replace an equivalent quantity of hay and concentrates on the basis of starch and protein equivalents. The essential features of the process for the preparation of the grass extract and extracted grass (which is a recent innovation) are the passage of the grass through a hot bath of juice from previous extractions, followed by crushing between rollers, and evaporation below 50° C. under reduced pressure to a syrupy consistence; the extracted grass is then dried and baled. Determinations were made of milk yield, butter-fat and solids-not-fat contents and examined statistically. The results showed that neither the extract nor the residual grass gave better results than the ordinary foods used in the control ration. Under the conditions of the experiment, however, it was not possible to attach any great significance to yield changes of less than 13·6, 9·7 and 2·0 per cent., respectively, in the above values. The mean carotene-contents of composite samples of extracted grass, hay and grass-extract (as determined by the method of Ferguson and Bishop, ANALYST, 1936, **61**, 515) were 9·70, 1·03 and 0·82 mg. per 100 g., respectively. Determinations of the carotene-content of the milk showed that there had been a significant response to the inclusion of extracted grass in the ration, although the grass-extract was without effect. It is concluded that for the partial replacement of an ordinary winter ration for dairy cows, extracted grass is as useful as young grass dried by orthodox methods. J. G.

Uronic Acid Content of the Nitrogen-free Extract of Feeding Stuffs. G. A. Guanzon and W. M. Sandstrom. (*J. Agric. Res.*, 1937, **55**, 581–586.)—The "residual nitrogen-free extract" (Fraps, *Tex. Agr. Expt. Sta. Bull.*, 1930, 418) is that part of the nitrogen-free extract remaining after the values for sugars,

starch and pentosans have been deducted, and includes the uronic acids which occur in the hemicellulose and pectic materials and in the cell walls of plants. The feeding stuffs examined were alfalfa hay, corn cobs, corn bran, peanut hulls, peanut kernels, rye, Timothy hay, wheat bran, and wheat shorts, representing concentrates, grain by-products and roughage. The air-dried samples (300 g.) were coarsely ground to pass through a sieve having circular openings of 1 mm. diameter. In determining uronic acid the method of Dickson, Otterson and Link (*J. Amer. Chem. Soc.*, 1930, **52**, 775) was followed, but the liberated carbon dioxide was received in two spiral tubes in series and the excess of barium hydroxide solution was titrated in these containers. The standard barium hydroxide solution was not introduced into the receiving train until the temperature of the reaction mixture was approaching 100° C., by which time (about 20 minutes) carbon dioxide due to carbonates had been removed. This is a slight modification of Anderson's method (*J. Biol. Chem.*, 1931, **91**, 559). Norris and Resch (*Biochem. J.*, 1935, **29**, 1590) have recently verified the statement that the determination of uronic acids by decarboxylation is quantitative. With the rye, wheat shorts and wheat bran, which contain much starch and sugars, a correction was made for the carbon dioxide evolved from these (0·45 per cent. of the weight of carbohydrate). Determinations of moisture, ash, crude protein, pentosans, sucrose, reducing sugars, starch and ether extract were made by the official methods of the A.O.A.C. Crude fibre was determined by the Kennedy modification (*Technical Methods of Analysis employed in the Laboratories of Arthur D. Little, Inc., Cambridge, Mass.*, Griffin, New York, 1921). Pentosans were also determined on the sample treated for weighing as crude fibre, and both pentosans and crude protein were determined on the fat-free sample which had been extracted for 30 minutes with boiling $N/50$ sulphuric acid and then for 15 minutes with sufficient boiling sodium hydroxide solution to give an $N/50$ concentration of alkali after neutralisation of the acid. The difference between the total pentosans and the pentosans in the crude fibre was considered to be the amount of pentosans in the nitrogen-free extract. The pentosans in the crude fibre were subtracted from the pentosans in the residue insoluble in $N/50$ acid and alkali, and the remainder was termed the insoluble pentosans in the nitrogen-free extract, the corresponding soluble pentosans being obtained by difference. From the value for the residue insoluble in $N/50$ acid and alkali was subtracted the sum of the values for crude fibre, crude protein and the pentosans in that insoluble residue. The remainder was termed the insoluble residual nitrogen-free extract, the value for the corresponding soluble residual nitrogen-free extract being obtained by difference. The pentosan-content of the crude fibre shows a closer relationship to the total crude fibre than does the uronic acid content, and this suggests that the variations in the uronic acid content are to be ascribed to the portion found in the nitrogen-free extract. Although there is no definite relationship between the uronic acid content and the total nitrogen-free extract, there is a tendency for them to vary inversely. In general, the percentage of uronic anhydrides is higher in roughages than in concentrates. Except with corn bran and peanut kernels the uronic acid content increases with the insoluble residual nitrogen-free extract, but no regularity appears when the soluble portion is considered. Digestibility coefficients calculated on the assumption

that sugars and starches are completely digested and the pentosans and nitrogen-free extract to the extent of their solubilities in $N/50$ acid and alkali, agree well with the results of feeding tests, especially with the concentrates. With the roughages the calculated coefficients are lower than those obtained by feeding tests. This suggests that the lower digestibility may be due, in part, to the high nitrogen-free extract, a portion of which is of a uronic acid nature. A. O. J.

Determination of Phosphoric Anhydride in Phosphate Rock, Superphosphate and "Metaphosphate." J. I. Hoffman and G. E. F. Lundell. (*Bureau of Standards J. Research*, 1937, **19**, 59–64.)—The authors propose to eliminate the customary preliminary precipitation of phosphorus as phosphomolybdate. Under proper conditions the phosphoric acid in a solution of phosphate rock or similar material can be determined by a process involving double precipitation of magnesium ammonium phosphate. *Method.*—A 0·5 g. sample is dissolved as completely as possible by boiling for 30 minutes with 15 ml. of hydrochloric acid and 3 ml. of nitric acid. The liquid is not filtered. With samples, such as "metaphosphates," yielding much gelatinous silica, it is preferable to digest the sample with 10 ml. of water, 5 ml. of hydrofluoric acid, and 20 ml. of nitric acid in a platinum dish. The liquid is then concentrated to 5 ml. by evaporation on a water-bath, the evaporation process being repeated after the addition of 10 ml. of water and 20 ml. of nitric acid; 50 ml. of dilute nitric acid (1 + 99) are added, and the liquid is heated on a water-bath for 10 minutes. To the solution of the sample obtained by either of these methods are added 30 g. of ammonium citrate, 10 ml. of hydrochloric acid, and 100 ml. of magnesia mixture (400 g. of magnesium chloride crystals and 300 g. of ammonium chloride dissolved in 1500 ml. of water, and the solution made alkaline with ammonia, filtered, and acidified with hydrochloric acid). The solution is made neutral to litmus with ammonia (sp.gr. 0·9), and 3 ml. are added in excess; it is diluted to approximately 250 ml., a few glass beads are added, and the flask is stoppered, mechanically shaken for half-an-hour, and then allowed to stand overnight. The precipitate is filtered off on a small paper of close texture, and the flask and precipitate are washed once with a little dilute (1+19) ammonia, the filtrate being discarded. The precipitate is dissolved from the flask and filter in about 50 ml. of warm dilute hydrochloric acid (1+4). The solution (100 ml.) is treated with 0·3 g. of citric acid and 1 ml. of magnesia mixture, then made alkaline to litmus with ammonia, added with stirring, and 5 ml. of ammonia are added in excess. The liquid is stirred occasionally during half-an-hour and allowed to stand for at least 4 hours. The precipitate is filtered off on a fine filter-paper, washed with dilute ammonia (1+19), the paper is ashed at a moderate temperature, and the precipitate is ignited at 1050° to 1100° C., yielding magnesium pyrophosphate. Iron, aluminium, titanium, silica, calcium, zinc, manganese, fluorine and organic matter, in the proportions found in phosphate rock, do not interfere. Only a part of the arsenic in the original material appears in the ignited precipitate; this is of no consequence, because 0·014 per cent. of arsenic is the highest proportion yet met with. If, however, much arsenic should be encountered, it should be removed by preliminary precipitation with hydrogen sulphide. The initial boiling during the process of dissolving the sample was

found to be satisfactory for converting any metaphosphate into orthophosphate. The fairly large amount of ammonium citrate was prescribed in order to prevent large amounts of iron and aluminium from interfering with the complete precipitation of phosphorus. The method is applicable to the analysis of liquids used with silicate cements in dentistry. S. G. C.

Water

Modification of the Palmitate Determination of Magnesia in Water. P. Hamer and H. E. Evans. (*J. Soc. Chem. Ind.*, 1937, **56**, 441T–442T.)—The method of Blacher (*Chem. Ztg.*, 1913, **37**, 56) for the determination of total and individual hardness in water consists of three stages, *viz.* (*a*) titration with acid to determine total alkalinity (corresponding with the temporary hardness in most waters), (*b*) subsequent titration of the solution freed from carbon dioxide with potassium palmitate (corresponding with the total hardness), and (*c*) determination in a fresh portion of the sample of the magnesium hardness by titration with potassium palmitate solution after precipitation of calcium by means of sodium oxalate. Difficulties due to the somewhat indefinite end-point have been encountered in the last stage, and a modification is recommended in which the magnesia is precipitated by sodium hydroxide, sodium aluminate being added as a coagulant and the lime hardness then determined. The water (100 ml.) is neutralised to methyl orange with 0·1 *N* hydrochloric (or nitric) acid, two drops of acid are added in excess, and the liquid is boiled to expel carbon dioxide. Phenolphthalein, followed by 6 ml. of 0·1 *N* sodium hydroxide in excess of the amount required to produce a pink colour, is added, boiling is continued for one minute in a covered beaker and, after the addition of 1 ml. of a 0·28 per cent. solution of sodium aluminate, the liquid is quickly cooled. The cold solution is titrated with 0·1 *N* acid until all trace of the pink colour has disappeared, and then with standard potassium palmitate, the end-point being the re-appearance of the pink colour of the phenolphthalein. The reading is taken when the first definite pink colour appears in the liquid. A further 0·1 ml. of the palmitate solution is then added and, if the colour is a deep pink, the first reading is the correct end-point. The same procedure should be followed when standardising the palmitate solution against barium chloride. If the total hardness of the water is below 5 parts of calcium carbonate per 100,000, 300 ml. of the sample are neutralised and concentrated by evaporation to 100 ml.; if the total hardness exceeds 40 parts per 100,000, the determination may be made with 50 ml. of the sample. The method was applied to a number of artificial waters containing from 1·5 to 51 parts per 100,000 of total hardness with varying ratios of lime and magnesia hardness, and the limits of the absolute error were −0·8 to +1·0 parts per 100,000.

A. O. J.

Gas Analysis

Note on the Use of the Haldane Apparatus for the Analysis of Gases containing Ether Vapour. J. C. Snyder. (*J. Biol. Chem.*, 1937, **122**, 21–25.)—Expired air containing ether vapour may be analysed with the ordinary Haldane

apparatus if the ether is first removed, by bubbling the air through conc. sulphuric acid. The gas-sampling tube is connected with the Haldane apparatus by means of a capillary U-tube, on each limb of which a bulb, of 0·75 ml. capacity, has been blown, so that the two bulbs are level. In addition, the limb connected with the Haldane apparatus has a second bulb, of 0·25 ml. capacity, above the first. Conc. sulphuric acid is placed in the U-tube so that the lower bulbs are half full; a very small drop of mercury in the capillary acts as a valve. Since sulphuric acid dissolves small amounts of oxygen, nitrogen and carbon dioxide, it is recommended that the acid should first be heated to 100–150° C. for 15 minutes, and then immediately before use saturated by exposing it to air of approximately the same composition as the sample to be analysed, or alternatively, by bubbling a few hundred ml. of the air to be tested through the acid in the capillary tube. The results agreed closely with those obtained by the standard method for ether-free air and by the use of acid with ether-free air and air containing 3 to 6 volumes per cent. of ether. There is little difference between the analyses of ether-free air with and without acid; the use of acid with samples containing 3 to 6 volumes per cent. of ether introduces an error of less than 1 per cent. for the oxygen-content and less than 5 per cent. for the carbon dioxide content. One great advantage of the method is that the apparatus is ready at once for accurate analysis of ether-free samples without replacement of solutions. F. A. R.

Rapid Method for the Accurate Determination of Helium (Neon) in Gas Mixtures. E. Schröer. (*Z. anal. Chem.*, 1937, **111**, 161–169.)—The author has modified the procedure of Paneth and Peters (*Z. physik. Chem.*, 1928, **A134**, 353) by adsorbing the other gases (nitrogen, oxygen, methane, etc.) on silica gel *in vacuo* in two stages instead of one. In the first stage the bulk of the other gases is adsorbed on about 10 g. of gel, capable of adsorbing 500 ml. of nitrogen at 0·25 mm. partial pressure. The gas is then admitted into a smaller absorption tube containing silica gel, in which the last of the nitrogen is eliminated. Its complete removal is ascertained by the disappearance of the nitrogen lines in the spark spectrum of the gas. When this has taken place, the volume and pressure of the residual gas are read. The original paper should be consulted for fuller details and the results of test analyses. W. R. S.

Organic

Determination of Deuterium in Organic Compounds. A. S. Keston, D. Rittenberg and R. Schoenheimer. (*J. Biol. Chem.*, 1937, **122**, 227–237.)—Several refinements have been introduced in the method of determining the deuterium-content of organic compounds. The sample under examination is placed in a platinum boat and burned in a quartz combustion tube loosely packed with copper oxide. The water formed during the combustion is collected in a U-tube immersed in solid carbon dioxide. When the combustion is complete, the trap is removed from the combustion tube and, if the presence of halogens is suspected, a piece of clean copper wire is added to the water. Excess of barium carbonate is then added to neutralise nitric acid. The trap is connected with a series of

three U-tubes, the first containing dry chromic oxide, and the second potassium hydroxide and potassium permanganate, the third being empty. The water is distilled *in vacuo* from one U-tube into the next, and finally from the third U-tube into a calibrated trap. It is removed from this trap as required by means of a fine pipette.

It is now the custom to determine both the refractive index and the density on each sample. If the results obtained differ by more than 0·02 atom of deuterium per cent., they are rejected and the water is re-purified. The difference in refractive index between the samples and pure water is determined with a Zeiss interferometer calibrated to read directly in per cent. of deuterium by means of samples of known deuterium-content. Determinations with an error of not more than 0·02 atom per cent. can be made on as little as 0·4 ml. of water. The most satisfactory routine method of determining the density of the water is the falling drop method. A drop of constant volume falls through a column of *o*-fluorotoluene, the temperature of which is kept constant by means of a thermostat, and the time taken to fall 15 cm. is measured by a stop-watch. *o*-Fluorotoluene has a density of 0·9996 at 26·8° C., and the density difference between it and water can be varied within reasonable limits, since the coefficients of thermal expansion of the two liquids are different. A difference in falling time of 1 second corresponds with about 2·5 parts per million in the density, equivalent to 0·002 per cent. of deuterium. Each drop measures only 7 c.mm. F. A. R.

Effect of Hydroxyl Groups on the Apparent Diene Values of Vegetable Oils and Fats. W. G. Bickford, F. G. Dollear and K. S. Markley. (*J. Amer. Chem. Soc.*, 1937, **59**, 2744–2745.)—A study of the applicability of the diene methods of Ellis and Jones and of Kaufmann, Baltes and Büter as a means of following changes in the polyethenoid linkages of soya-bean oil confirmed the fact that during solidification of the oil on heating, anomalous diene values are obtained in the presence of hydroxyl groups. The maleic anhydride and diene values of a number of purified hydroxylated compounds were determined before and after "blocking" the hydroxyl groups by acetylation. The compounds examined included methyl 12-hydroxystearate, glyceryl monoricinoleate, α-monopalmitin, etc. In every instance but one (α,α′-distearin), significant diene and maleic anhydride values were observed with the hydroxylated compounds, but practically zero values after acetylation. Several oils (soya-bean, linseed, castor, perilla, oiticica and tung) were similarly examined. Castor oil showed the characteristic behaviour of hydroxy compounds, the value falling nearly to zero after acetylation; tung oil showed a small decrease in values, but for linseed and soya-bean oils the values increased after acetylation. The increase in diene values was accompanied by an increase in refractive indices, a decrease in iodine values, and a shortening of the drying time, indicating a shift of the polyethenoid bonds towards a conjugated system. D. G. H.

Test to Distinguish between Wool and Casein Fibre. C. M. Whittaker. (*J. Soc. Dyers and Colourists*, 1937, **53**, 468.)—If wool and casein fibre (*e.g.* "Lanital") are immersed for 1 minute in a cold solution of 0·5 g. of one of a number

of wool dyestuffs (*e.g.* Xylene Light Yellow 2 G, Azo Geranine 2 GS or Erio Fast Cyanine S conc.) in a mixture of 0·5 ml. of 80 per cent. sulphuric acid and 100 ml. of water, the former is only slightly stained, whereas the latter is dyed to a full shade. If the fabric under examination is dyed and contains both of the above types of fibre, the dyestuff reagent chosen should be such that its colour contrasts with that of the fabric; the relative distribution of the two fibres may then be seen either with the naked eye or under the microscope. The test is equally effective with chlorinated wool. Neocarmine W stains undyed casein fibre and wool deep orange and bright yellow, respectively; on undyed chlorinated wool it produces a fuller shade of bright yellow. In ultra-violet light undyed wool has a weak violet fluorescence, whilst undyed casein fibre has a dead white shade. J. G.

Oxidation of some Polyhydroxylic and Polyethylenic Higher Fatty Acids by Aqueous Alkaline Permanganate Solutions. T. G. Green and T. P. Hilditch. (*J. Chem. Soc.*, 1937, 764.)—When oxidised with aqueous alkaline permanganate under specified conditions (*cf.* Lapworth and Mottram, *J. Chem. Soc.*, 1925, **127**, 1987), 9:10-dihydroxystearic acid (m.p. 131° C.) yields suberic, octoic and oxalic acids. Under similar conditions this type of oxidation also occurs with 9:10-dihydroxystearic acid (m.p. 95° C.), 9:10-dihydroxypalmitic acids (m.p. 123–4° C. and m.p. 83° C.), 13:14-dihydroxybehenic acids (m.p. 128° C. and m.p. 100° C.) and 6:7-dihydroxystearic acid (m.p. 122° C.). The oxidation is thus independent of the stereoisomeric form of the acid, the length of the carbon chain, or the position of the adjacent hydroxyl groups in the chain, and it is not influenced by temperature. Resistance of these acids to oxidation increases with the distance between the carboxyl and hydroxyl groups. The concentrations of the aqueous solutions used were somewhat greater than those used by Lapworth and Mottram (*loc. cit.*), and the initial procedure was as follows:—A solution of 20 g. of potassium permanganate in 1500 ml. of water at 0° C. was added to a solution of 5 g. of the dihydroxy acid and 14 g. of potassium hydroxide in 2000 ml. of water at the same temperature. After standing for $2\frac{1}{2}$ hours at room temperature, the mixture was decolorised with sulphur dioxide, and 100 ml. of conc. hydrochloric acid were added. Lapworth and Mottram's procedure was then followed. The dibasic acids obtained were, in general, purified by re-crystallisation from chloroform. Suberic acid, which is only very slightly soluble in chloroform, was re-crystallised from water if necessary. When the tetrahydroxystearic acids (m.p. 155° C. and m.p. 173° C.), and the hexahydroxystearic acids (m.p. 169° C. and 203° C.) were oxidised similarly, but with double the amounts of permanganate and alkali, the dicarboxylic acids formed were azelaic acid (about 80 per cent.) and suberic acid (about 20 per cent.). Azelaic acid is much more soluble in chloroform than is suberic acid. The dibasic acids from the similar oxidation of α- and β-elaeostearic acids (using three times the original amount of permanganate and alkali) consisted also of approximately 80 per cent. of azelaic acid and 20 per cent. of suberic acid. These results indicate that alkaline permanganate oxidation may not always be satisfactory for determining the position of ethylene linkages in long-chain compounds.

Fatty Substances of Japanese Wild Bees and their Combs. S. Ueno and S. Komori. (*J. Soc. Chem. Ind., Japan,* 1937, **40**, 432–434B.)—The fatty acids extracted with ligroin from the combs of three species of Japanese wild bees had the following analytical values:

	Vespa mandarina	*Vespa crabroniformis*	*Polistes yokohamae*
n_D^{60}	1·4572	1·4568	1·4557
Sp.gr. at 60°/4° C.	0·8877	0·8757	0·8668
Acid value	153·2	83·0	121·8
Saponification value.. ..	173·0	139·8	132·0
Iodine value (Wijs)	69·9	67·1	77·4
Unsaponifiable matter, per cent.	22·93	27·58	—

The percentages of fatty substances present in the combs were:—*Vespa mandarina*, 10·6; *Vespa crabroniformis*, 6·0; *Polistes yokohamae*, 5·7. The comb oils of the three species resemble one another. Their fatty acids consist chiefly of palmitic, oleic and linolic acids. The unsaponifiable matter contains cholesterol and hydrocarbons. The test for alkaloids in the comb of *Vespa mandarina* was negative, although this comb is used in Chinese medicine.

Oil extracted with ether from the pupa of *Vespa mandarina* had the following characteristics:—n_D^{20}, 1·4635; sp.gr. at 20°/4° C., 0·9145; acid value, 19·5; saponification value, 181·3; iodine value, 71·3; unsaponifiable matter, 5·99 per cent.; solid part of mixed fatty acids, 54·7 per cent. This iodine value is lower, and the content of solid fatty acids is higher than in other insect oils. These comb oils differ from common beeswax in not containing higher saturated acids.

E. B. D.

Gravimetric Bromine Values of some Fatty Oils. E. Yamaguti, T. Matsushima and T. Takagi. (*Memoir, Faculty Science, Waseda University, Tokyo, Japan,* 1937, No. 12, p. 118.)—In place of the smooth glass plates used in the "bromine vapour weighing" method for the determination of the bromine value (Becker, *Z. angew. Chem.*, 1923, 539; Toms, ANALYST, 1928, **53**, 69), the authors used ground-glass discs with rounded and slightly turned-up edges, with a view to ensuring evenly coated oil films (about 9 cm. in diameter). Olive, tsubaki, arachis, rapeseed, soshi, whale, sardine and liver oils, tallow and lard gave bromine values corresponding fairly well with the Wijs iodine values. The following oils gave values inconsistent with the Wijs values (the figures show the difference between 126·92 × bromine value/79·92 and the Wijs value):—sesame, soya-bean, linseed, geihi, and hardened soya-bean oils (2 to 6); castor oil (7 to 8); polymerised sardine oil (about 20, the discrepancy depending on the degree of polymerisation); Japanese and Chinese wood oils (about 40 and 70 respectively). E. M. P.

Inorganic

Reactions of Cations and Anions with Tri-hydroxy Aromatic Compounds. P. Wenger, R. Duckert and C. P. Blancpain. (*Helv. Chim. Acta,* 1937, **20**, 1427–1445.)—Comparative tests have been carried out of the reactions of

a range of metallic salts in dilute aqueous solution with the following compounds:—1, 2, 3-trihydroxybenzene (pyrogallol); 1, 2, 4-trihydroxybenzene (hydroxyhydroquinone); 1, 3, 5-trihydroxybenzene (phloroglucinol); 9-methyl-2, 3, 7-trihydroxy-6-fluorone. The principal interest was attached to the precipitation of a coloured precipitate from a weakly acid solution. *Pyrogallol.*—The only elements giving precipitates were antimony (acid solution) and bismuth and titanium (buffered acetate solution); iron and osmium gave coloured solutions. There were no notable reactions with anions, excepting possibly a colour with the titanate ion. *Hydroxyhydroquinone.*—None of the characteristic precipitates given by pyrogallol was produced. A colour was given with osmium in acid solution; a precipitate with osmium, a greenish-blue colour with ferrous iron, and a bluish-gray precipitate with ferric iron were given in buffered acetate solution. The iodate anion in alkaline solution gave a carmine colour which turned black on neutralisation. *Phloroglucinol.*—The arsenic group of metals gave colours in alkaline solution, but not precipitates analogous to those produced with pyrogallol. On the other hand, precipitates were given by ceric salts in acid, and stannous salts in alkaline solution; bivalent palladium gave a colour in both acid and alkaline solution; ferric iron and osmium also gave colours, the former in acid and the latter in alkaline solution. The following two anions gave reactions of special interest: bromate—yellowish-brown precipitate (acid solution), nitrite—yellow colour (acid solution). *9-Methyl-2, 3, 7-trihydroxy-6-fluorone.*—Brownish or reddish precipitates were given as follows:—tervalent titanium and cerium, germanium, arsenic antimony, bivalent chromium, sexavalent molybdenum and tungsten, and quadrivalent uranium (acid solution); bismuth (almost neutral solution). Many elements gave precipitates in alkaline or in buffered acetate solution (*cf.* Abst., ANALYST, 1937, **62**, 574). S. G. C.

Determination of Manganese in Cobalt-Chromium Steels by Photometric Titration. S. Hirano. (*J. Soc. Chem. Ind. Japan*, 1937, **40**, 412–413B.)—The method was devised to overcome difficulties in the usual method occasioned by the presence of cobalt and chromium. The manganese in solution is oxidised with potassium bromate, and the permanganate formed is determined photometrically (*cf. id.*, 1934, **37**, 177B; Abst., ANALYST, 1934, **59**, 573). A suitable condition for the titration is that 100 ml. of the steel solution should contain 50 to 60 ml. of conc. sulphuric acid and 10 to 30 ml. of phosphoric acid (90 per cent.) at a temperature below 40° C. The steel sample is dissolved in dilute (1:4) sulphuric acid; the ferrous iron is oxidised with hydrogen peroxide, the excess being removed by boiling. Carbonaceous matter is oxidised with ammonium persulphate (1 g.), and the solution is boiled for a further 15 minutes. The required quantities of sulphuric and phosphoric acids are added, the solution is cooled and titrated photometrically with $N/30$ potassium bromate solution. As the manganese is not completely oxidised to permanganate, the manganese equivalent of the bromate solution must be determined empirically by standardisation against a standard steel. Good results were obtained in tests with solutions of standard carbon steels to which solutions of various alloying elements were added, and also with steels containing up to 4 per cent. of cobalt, 13·5 per cent. of chromium

and 2 per cent. of tungsten. When chromium was present, the chromic acid formed in the ammonium persulphate oxidation was reduced by subsequently adding sufficient hydrogen peroxide, the excess of which was destroyed by boiling. Tungsten steel was dissolved as completely as possible in a mixture of sulphuric and phosphoric acids. Nitric or hydrochloric acid must be absent from the solution titrated. S. G. C.

Determination of Zirconium in Ferro-zirconium by means of Sodium Methylarsinate. R. Chandelle. (*Bull. Soc. Chim. Belg.*, 1937, **46**, 423–427.)—The finely-powdered alloy (0·3 g.) is fused with 4 to 5 g. of sodium peroxide in a nickel crucible. The fused mass is extracted with 300 to 400 ml. of hot water, the insoluble residue is left to settle, and the solution is filtered; the residue is washed by decantation until free from alkali, and dissolved in 5 *N* hydrochloric acid. The solution is evaporated to dryness, the residue is dissolved in 60 ml. of hydrochloric acid (sp.gr. 1·10 to 1·115), and the iron is removed by extraction with ether. The aqueous layer is evaporated to a syrup, diluted with 0·5 *N* hydrochloric acid to 250 ml., and a filtered aliquot portion containing about 0·03 g. of zirconium is treated as described in the earlier paper (Abst., ANALYST, 1937, **62**, 899). W. R. S.

Microchemical

Determination of Magnesium in Milk Products by a Micro-method. J. H. Bushill, L. H. Lampitt and D. F. Filmer. (*J. Soc. Chem. Ind.*, 1937, **56**, 411T–413T.)—The ash of a sample corresponding with about 2 g. of milk solids is dissolved in 0·5 *N* hydrochloric acid, filtered if a silica ashing dish has been used, diluted to about 90 ml. with water, and treated with sufficient 0·5 *N* hydrochloric acid to bring the *p*H below 1·2 (red to thymol blue). After the addition of 7 ml. of 6·4 per cent. oxalic acid solution the mixture is heated almost to boiling, and *N* ammonia solution is added, drop by drop, until the solution is yellow (*p*H 3). The solution is then heated on a boiling water-bath for 3 hours, cooled and, within half-an-hour of cooling, the precipitate is collected on a filter-paper (9 cm. Whatman 41), and washed until free from chlorides, with ammonium oxalate solution (5 ml. of 6·4 per cent. oxalic acid solution diluted to 100 ml. and adjusted to *p*H 3 by the addition of *N* ammonia solution). Calcium may be determined in the precipitate if required (Lampitt and Bushill, *Biochem. J.*, 1934, **28**, 1305; Abst., ANALYST, 1934, **59**, 828; 1935, **60**, 195). The filtrate and washings contain the whole of the magnesium. After the addition of 2 ml. of 7·5 per cent. potassium dihydrogen phosphate solution in 10 *N* sulphuric acid, the solution containing the magnesium is evaporated, the residue is ignited cautiously until fuming ceases, 10 ml. of *N* hydrochloric acid are added, and the solution is evaporated to dryness. The residue is dissolved in a definite volume (usually 20 ml.) of 0·1 *N* hydrochloric acid, the volume being such that 1 ml. contains about 0·1 mg. of magnesium. To 1 ml. of the solution in a conical flask are added 3 drops of 2 *N* ammonium chloride solution, 1 ml. of *M*/3 disodium phosphate and a drop of 0·5 per cent. phenolphthalein solution. One ml. of 10 per cent. aqueous ammonia solution in excess of that required to make the solution pink is then added, and the sides

of the flask are immediately scratched with a glass rod for 1 minute, after which the solution is set aside for about 18 hours at 0° C. to 5° C. The precipitate is collected on a 15 A.G.4 Jena glass filter, the flask and filter being washed with four 5-ml. portions of 0·3 per cent. aqueous ammonia solution followed by three 10-ml. portions of 96 per cent. alcohol. The precipitate on the filter and in the flask is dissolved in 2 ml. of *N* hydrochloric acid and rinsed with hot water into a suitable receiver, the combined filtrate and washings are evaporated to dryness on the water-bath, and the residue is dissolved in 10 ml. of *N* sulphuric acid. Aliquot portions (2 ml.) of this solution are used for phosphorus (and therefore magnesium) determination by a molybdenum-blue colorimetric method (Kuttner and Lichtenstein, *J. Biol. Chem.*, 1930, **86**, 671). To the solution are added 5·2 ml. of distilled water, 0·8 ml. of 10 *N* sulphuric acid and 1 ml. of sodium molybdate solution. A standard phosphate solution (2 ml.) is simultaneously treated with 5 ml. of water, 1 ml. of 10 *N* sulphuric acid, and 1 ml. of the sodium molybdate solution. After an interval of 2 minutes 1 ml. of stannous chloride solution (*vide infra*) is added to each solution, and after a further interval of 1 minute the colours developed are matched in a colorimeter. By suitable adjustment of the standard phosphate solution to yield a colour approximating in intensity to that of the test solution, the experimental error can be reduced to ±2 per cent. The glass apparatus used should be kept in chromic acid solution when not in use. The reagents used in the colorimetric method are prepared as follows:—standard phosphate solution: 0·4385 g. of potassium dihydrogen phosphate in 1 litre of water (1 ml. = 0·100 mg. P), diluted as required, usually so that 2 ml. = 0·025 mg. P = 0·0196 mg. Mg; sodium molybdate solution: a 7·5 per cent. solution of the "pure" salt is kept for 3 or 4 days and filtered before use; stannous chloride solution: a stock 40 per cent. solution of stannous chloride in conc. hydrochloric acid is kept in the dark at 0° C. to 5° C. and diluted 200-fold as required. The following are the amounts of magnesium, in p.p. 100,000, found in some dairy products:—separated milk, 10·1; cream (50 per cent. fat), 6·1; ice-cream (fat 13·0, milk S.-N.-F. 10·3 per cent.), 15·0; Gruyère cheese (fat 23·8, total solids 53·6 per cent.), 30·9; Cheddar cheese (fat 41·2, total solids 73·1 per cent.), 30·7; Parmesan (fat 24·4, total solids 75·8 per cent.), 47·3. A. O. J.

Micro-determination of Total Alkali and the Gravimetric Determination of Sodium as Sodium-magnesium Uranyl Acetate. Application to the Analysis of Mineral Waters. R. Dwonzak and A. Friedrich-Liebenberg. (*Mikrochimica Acta*, 1937, **1**, 168–193.)—Experiments carried out to define the conditions under which the chlorides and sulphates respectively of the alkali metals (lithium, sodium and potassium) represent suitable forms for weighing, show that the chlorides of the three metals are all stable at 200° C.; sodium and potassium chlorides are not appreciably hygroscopic, but lithium chloride is extremely so, and is therefore unsuitable for gravimetric determination. All the three sulphates are stable up to 700° C. and on heating salts of the three metals with sulphuric acid to 700° C. all are converted entirely into the neutral sulphates; the addition of ammonium carbonate, as often recommended, is quite superfluous. *Total alkali in mineral waters.*—A few ml. of the water are evaporated

with hydrochloric acid to render the silica insoluble, then the other ions, with the exception of the alkalis, are precipitated by boiling for about half-an-hour with calcium hydroxide (about 0·12 g. CaO in 10 ml. of water). The excess of calcium hydroxide is subsequently removed first by precipitation as carbonate and finally as oxalate; platinum filter-sticks are used for the filtrations. In the final filtrate the alkalis are converted into the sulphates by evaporation with sulphuric acid and heating to about 700° C. in a platinum crucible. The analysis takes about 6 hours. The result must be corrected for the alkali-content of the calcium hydroxide. Results on about 5 mg. of total alkali gave errors varying from −0·88 and +0·52 per cent.

Determination of sodium as sodium magnesium uranyl acetate.—The best concentration of the sample for precipitation lies between 0·3 and 0·025 mg. of sodium per ml. The reagent consists of 32 g. of uranyl acetate (cryst.), 100 g. of magnesium acetate and 20 ml. of acetic acid dissolved on the water-bath in a mixture of 500 ml. of alcohol and 300 ml. of water, diluted with water to 1 litre, and filtered after 48 hours. For the precipitation of 1 mg. of sodium the theoretical amount of reagent required is 1·588 ml., but for the best results about an 8 times excess is required. For completely unknown amounts of sodium it is best to obtain first a rough approximation. The solution and reagent should be mixed and left for 16 hours for complete precipitation. The precipitate is washed twice with reagent and finally 4 or 5 times with a little alcohol, and dried at 110° C. Jena glass filter-beakers are used for the determination. Excellent results are obtained on pure solutions of sodium salts. In the presence of 8 times the amount of potash large errors (up to +20 per cent.) may be obtained, but as much as twice the amount may be present without danger. Lithium salts interfere when more than equal amounts of the two salts are present. Calcium and barium salts do not interfere up to 11 times the amount of sodium present. An equal amount of iron salts does not interfere. Phosphates are usually present in mineral waters only in small concentration; in amounts up to 10 per cent. of the quantity of sodium present they do not interfere. Soluble silicate, up to 8·5 times the amount of the sodium present does not interfere with the determination, so that sodium may be determined directly in mineral waters, excellent results—rather better than on the macro-scale—being obtained. J. W. M.

Method for the Determination of Small Amounts of Phosphate by the Use of 8-Hydroxyquinoline. E. J. King and G. E. Delory. (*Biochem. J.*, 1937, **31**, 2046–2048.)—An amount of the solution containing 2–10γ of phosphorus is measured into a conical 15 ml. centrifuge tube and water is added to 5 ml. One ml. of Berg's "oxin-molybdate" solution is added, and the mixture is shaken. The tube is then immersed in water at 60° C. for 30 minutes to cause the precipitate of 8-hydroxyquinolinephosphomolybdate, $(C_9H_7ON)_3H_7[P(Mo_2O_7)_6].2H_2O$, to flocculate. The tube is then centrifuged for 5 minutes, the supernatant solution is decanted, and the tube is allowed to drain as dry as possible. Five ml. of ice-cold water are blown into the tube from a fine-tipped pipette, the tube is again centrifuged, and the supernatant liquid is poured off as before. The precipitate is then dissolved in 5 ml. of 0·1 *N* sodium hydroxide solution. 0·5 ml. of Folin–Ciocalteu phenol reagent (*J. Biol. Chem.*, 1927, **73**, 627) is added and 2 ml. of

10 per cent. sodium carbonate solution. After mixing, the tube is placed in water at 40° C. for 10 minutes to allow the blue colour to develop. Two standard phosphate solutions are prepared. One, made by dissolving 2·194 g. of pure potassium dihydrogen phosphate in 500 ml. of water, contains 1 mg. of phosphorus per ml.; the other, made by diluting 2 ml. of the first solution to 1 litre with water, contains 2γ per ml. Both are kept saturated with chloroform to prevent bacterial growth. The "oxin-molybdate" solution is made by dissolving 0·8 g. of 8-hydroxyquinoline and 4·2 g. of ammonium molybdate separately in 5 *N* hydrochloric acid, mixing, and making up to 100 ml.

Folin and Ciocalteu's phenol reagent is made by dissolving 50 g. of sodium tungstate and 12·5 g. of sodium molybdate in 350 ml. of water, together with 25 ml. of 85 per cent. phosphoric acid and 50 ml. of conc. hydrochloric acid. The mixture is boiled under a reflux condenser for 10 hours, after which 75 g. of lithium sulphate and 25 ml. of water and a few drops of liquid bromine are added. The mixture is boiled gently without reflux for 15 minutes to remove excess of bromine, then cooled, diluted to 500 ml., and filtered if not perfectly clear. The solution should be preserved in a glass-stoppered brown bottle.

In test experiments in which quantities of 2·5γ and 5γ of phosphate were added to blood plasma (7·3 and 9·9 ml.) the quantities recovered were 2·5γ and 5·1γ. These are typical of many other results.

In determining organic phosphate, a measured amount of the solution is placed in a conical 15-ml. centrifuge tube and digested with 0·2 ml. of 60 per cent. perchloric acid over a micro-burner. The possibility of bumping is minimised by heating the tube a short distance from the burner and by the introduction of a fine glass rod with a small indentation at the lower end. The mixture first turns brown and then becomes colourless when oxidation is complete. The glass rod is washed with about 3 ml. of water, the acid is neutralised with 2 ml. of *N* sodium hydroxide solution, oxin-molybdate is added, and the determination is carried through as described above. The results were in close agreement with the theoretical.

To estimate the inorganic phosphate in blood, 0·1 ml. of the sample is washed into 5·4 ml. of water, and 2 ml. of trichloroacetic acid are added. The mixture is shaken and filtered, 5 ml. of the filtrate and 1 or 2 ml. of the phosphate standard are placed in conical centrifuge tubes, and the determination is carried out as described above. The organic phosphate is determined after digestion of 1·0 ml. of the above-mentioned filtrate with 0·2 ml. of perchloric acid. The results corresponded closely with those given by King's (*Biochem. J.*, 1932, **26**, 292) modification of the method of Fiske and Subbarow (*J. Biol. Chem.*, 1925, **66**, 375).

F. A. R.

Investigations on the Determination of Micro-quantities of Iodine. J. F. Reith and C. P. van Dijk. (*Biochem. J.*, 1937, **31**, 2128–2135.)—Methods are described for quantitatively converting the iodine present in such materials as water and urine into a form suitable for determination by the azide-bromine-sulphuric acid method previously described by Reith (*Biochem. Z.*, 1935, **279**, 203). Traces of iodide can be quantitatively extracted from a solution (not more than

5 ml.) of salts, in which potassium carbonate (about 2 g.) preponderates, by means of two extractions with 5 ml. of 93 per cent. alcohol. Other salts are extracted in such small amounts that they do not interfere with the titration. The use of formic acid to remove traces of bromine from solution before titration is not recommended. Iodate is quantitatively reduced to iodide, which can then be determined by extraction and titration, by boiling 50 ml. of the solution, containing about 10γ of iodine, with 20 mg. of hydrazine hydrate and 1 mg. of potassium carbonate for 30 minutes. Reduction to the extent of 90 per cent. occurs when the solution is merely evaporated to dryness. No detectable amount of iodate is formed when iodide is heated at 500° C. for 30 minutes with potassium carbonate and sodium nitrate. Small amounts (50 mg.) of organic matter can be destroyed with practically no loss of iodide by heating with excess of nitrate. A simple and cheap bronze block furnace, heated by means of three Teclu burners, for igniting dishes to temperatures up to 550° C. is described. By using this furnace, platinum dishes can be replaced by porcelain. F. A. R.

Benzidine Method for the Micro-determination of Sulphate. Application to the Determination of Total Sulphur in Soil Solutions, Extracts, etc. A. W. Marsden and A. G. Pollard. (*J. Soc. Chem. Ind.*, 1937, **56**, 464–468T.)—By careful adjustment of the *p*H, quantity of reagent, temperature, reaction period and washing conditions, and by eliminating the interfering effects of certain salts (notably chlorides, phosphates and nitrates), sulphates may be precipitated quantitatively as benzidine sulphate, which may then be titrated with potassium permanganate. Existing methods in which the sulphate in the precipitate is titrated are unsuitable if less than 1 mg. is present; and colorimetric methods of determining the benzidine are influenced by the presence of small amounts of iron, manganese or aluminium. In the proposed method a quantity of sample (*e.g.* soil) containing 0·05 to 2·0 mg. of sulphate is evaporated in a hard-glass dish with 0·5 ml. of conc. nitric acid, and the residue is moistened with the acid and again evaporated; silica or porcelain dishes are unsuitable, as they occlude some of the sulphate. The dish is then placed in an electric oven at 400° C. for 1 hour in order to remove organic matter, and the new residue is again moistened with nitric acid, which is removed on the water-bath. This operation is then repeated with the use of hydrochloric acid, and the final residue is warmed on the water-bath with 2 ml. of water and 1 drop of 0·1 *N* hydrochloric acid. The contents of the dish are then washed into a pointed, graduated centrifuge tube (capacity, 8 ml.), three 0·5-ml. portions of water being used for washing, and the volume is made up to 4 ml.; the *p*H of the solution should be about 3. One ml. of a freshly-prepared filtered 0·8 per cent. solution of benzidine hydrochloride is added, and 5 minutes later the tube is immersed in a mixture of crushed ice and water for 10 minutes. It is then centrifuged for 5 minutes at 3000 r.p.m., after which the supernatant liquid is decanted and the residue washed with 5 ml. of 80 per cent. alcohol. The centrifuging, decantation and washing are repeated twice more, the last traces of alcohol being removed by placing the tube in hot water, and the residue is then dissolved in 5 ml. of a 0·5 per cent. solution of potassium hydroxide. The liquid is washed into a flask, four 5-ml. portions of water being used, 1 ml. of conc.

sulphuric acid is added, and the solution is titrated while hot with a 0·05 *N* solution of potassium permanganate. When the apparent end-point is reached, an excess equal to one-fourth of the volume used, and an extra 1·0 ml. are added, followed after 10 minutes on the water-bath by 2·0 ml. of 0·05 *N* sodium oxalate solution. When the precipitated manganese has dissolved, the titration is completed with the permanganate solution; the total titration figure, minus 2, and multiplied by 0·118, gives the number of mg. of sulphate (SO_4'') present. The maximum differences in SO_4'' content compared with those obtained by precipitation with barium chloride ranged from −10 to +9 p.p.m. for 100 ml. of soil solutions containing 200 to 800 p.p.m. of SO_4''. If coal-gas flames are used for heating purposes at any stage of the method, positive errors result. With Cl:S ratios considerably in excess of those found in most soil extracts, and if no more than 0·06 mg. of PO_4''' or 1 mg. per ml. of NO_3' is present, the errors due to these cations are negligible. J. G.

Detection of Oxalic Acid in Leather. K. Klanfer and A. Luft. (*Mikrochimica Acta*, 1937, **1**, 142–144.)—The detection of oxalic acid by the formation of aniline blue, as described by Feigl and Frehden, can be carried out directly on the samples of leather. A small amount of diphenylamine (about 0·2 g.) is pressed on to the sample of leather, melted by gently heating with a micro-flame from above, and maintained in the liquid state for about 1 minute. Two or three drops of alcohol are then dropped on to the spot, and the sample is left in a light place. The appearance of a blue colour indicates the presence of oxalic acid. When the test is carried out on pure oxalic acid in a crucible the blue colour appears at once after the addition of alcohol, but in leather the colour appears only after 1 or 2 hours, when large amounts of oxalic acid are present and after as long as 10 hours with traces, so that an approximate estimate of the amount of oxalic acid present may be made. J. W. M.

Reviews

ELASTICITY, PLASTICITY AND STRUCTURE OF MATTER. By R. HOUWINK Pp. xviii+376. Cambridge University Press. 1937. Price 21s. net.

This volume should take its place as one of the most important of the scientific texts published during the year 1937. For long enough the physicist and the applied mathematician have studied the elastic and viscous properties of matter, and have endeavoured, with varying success, to subsume the facts of experiment under some comprehensive equation of state or similar formula. The work of the applied mathematician, in particular, though regarded as being, in some respects, out of touch with reality, yet furnished methods of attack and results of very high value in the classical problems of large-scale engineering.

But the chemist and the scientific technologist whose work trenches upon chemical problems have during the last generation accumulated experimental results in this domain at a rate that is positively bewildering, and it is only within recent years that our rapidly increasing knowledge of the intimate structure of

matter has enabled these investigations, of high technical importance, to be absorbed into the present content of physical theory—theory which is now developed in such a manner as to react on, and add to, the mass of technical knowledge that already exists.

A complete catalogue of the topics handled in the book would exceed the length allotted to its review. It is only possible to say briefly that about 130 pages are devoted to four general chapters dealing with the elastic and plastic behaviour of matter, the relation of such behaviour to the internal structure of matter, the conditions for the elastic and plastic behaviour of matter, and to a valuable chapter on the plasticity of crystals, contributed by Dr. W. G. Burgers.

The remaining chapters of the book deal with the properties and structure of amorphous substances, such as glasses and resins, of rubber, cellulose and its derivatives, proteins, bakers' dough, paints and lacquers, clay and sulphur.

The book is fully documented, is a treasure house of facts, is concerned more with the results of mathematical analysis than with the details of that analysis, and may fairly be classed among the indispensables. A. FERGUSON

ORGANIC CHEMISTRY. By FRANK C. WHITMORE. Pp. x + 1080. London: Chapman & Hall, Ltd. 1937. Price 40s. net.

This work, by the President-Elect of the American Chemical Society, is intended as a one-volume reference book for practising organic chemists and for students who have already acquired some general knowledge of the subject. It succeeds admirably in its purpose, for it is full of useful information set out in a clear and concise manner, and its utility is considerably enhanced by the provision of a full and carefully compiled index running to 120 pages.

Much new work published during the last 15 years has been incorporated in the text, and numerous references are given to the Annual Reports published by our Chemical Society.

Of particular utility, because they are otherwise difficult of access, are the copious references to the methods of production of those extensive and rapidly growing groups of substances obtained by the industrial application of modern catalytic processes or derived from unsaturated hydrocarbons produced during the "cracking" or thermal decomposition of the higher-boiling fractions of petroleum.

Non-industrial chemists will find scattered throughout the book answers to various questions which must have puzzled them—or their enquiring students—from time to time; the present reviewer, who has occasionally wondered how methylene chloride comes on the market at quite a low price, had his mind set at rest on finding (p. 92) that chloroform is now prepared by the reduction of carbon tetrachloride by means of moist iron and that methylene chloride is an obvious by-product.

Here and there in the text are to be found definite statements which, possibly through the necessity for brevity, are rather in advance of experimental verification; for example, it is stated (p. 338) that esterification and hydrolysis take place "through an addition to the carbonyl group" (it is only fair, however, to add that on p. 126 this process is referred to as a "conception"), (p. 451) that oxalic acid "crystallises as the ortho-acid, $(HO)_3C.C(OH)_3$," and (p. 232) that formaldehyde

phenylhydrazone exists in α- and β-forms. It only remains to add that the publishers have done their part in an admirable manner—the pages are opaque and the type clear and distinct. J. KENYON

A SHORT HISTORY OF CHEMISTRY. By J. R. PARTINGTON, M.B.E., D.Sc. Pp. 386. London: Macmillan & Co., Ltd. 1937. Price 7s. 6d.

Professor Partington's "A Short History of Chemistry" is a text-book for the use of those preparing for a science degree in universities, where a knowledge of the historical sequence of discoveries and development of ideas in chemistry is expected of candidates.

The first third of the book is devoted to pre-Lavoisier Chymistry because the author considers that lecture courses deal with many of the notable features of later discoveries, so that less emphasis on them is needed in a book of this kind, except perhaps in Physical Chemistry. In the main, the author's method of writing history is to mention the leading figures of each era and to state concisely what each has contributed to theory or experiment. This is perhaps the easiest way of answering the question: What did so-and-so think?—but it is a method somewhat inadequate to answer the more important one: Why did so-and-so believe this, which seems so improbable to a chemist of the twentieth century? Limitations of space make it difficult to include all those who have had a decided influence on chemical thought and yet to write in an interesting manner about the "Why?" of their philosophies.

Professor Partington has certainly cast his net wide, and the scope is certainly wide enough for the most exacting critic, as can be seen from the list of names; under N, for example, are listed: Nagarjuna, Neri, Nernst, Neumann, Neustadt, Newlands, Newton, Nicolaus of Cusa, Noddack, and Noyes—a list formidable enough to put temptation in the way of the examiners! And most of the other letters of the alphabet have even longer lists and even less familiar names. Proverbially, one man's meat is another's poison, and educationally the reviewer is not partial to potted meat, under which category most of this book undoubtedly falls; for it is a text-book rather than one for light pleasurable reading. It is, however, well illustrated by a number of instructive plates and a collection of splendid portraits, and it will indeed meet the needs of those who require their information condensed into the smallest possible number of pages, and at a very reasonable cost. T. H. READE

THE CHEMISTRY AND TECHNOLOGY OF RUBBER. Edited by C. C. DAVIS; Associate Editor, JOHN T. BLAKE; with thirty-nine Contributors. American Chemical Society Monograph. Pp. 898. New York: The Reinhold Publishing Corp.; London: Chapman & Hall, Ltd. 1937. Price 75s. net.

The publication of books on the chemistry and technology of rubber may soon approach the same condition as is said to exist in fiction; there will be more people writing them than reading them!

The present volume, however, is very welcome. It has the stamp of authority of the A.C.S. Monograph series, which is augmented by the eminence of the editors and contributors, and it makes a useful addition to the literature on rubber.

The thirty-nine contributors provide between them twenty-five chapters dealing in an orthodox manner with all the aspects of rubber chemistry and technology. Dr. van Rossem opens with a chapter on the composition of crude rubber. Latex is dealt with later (Chapters XVI and XVII). Physical properties and chemistry of raw rubber are to be found in Chapters II and III; mastication and solvation follow, and then comes vulcanisation theory by Ira Williams. This chapter is a valuable and lucid review of the subject; particularly interesting is this author's view that polymerisation plays little or no part in the vulcanisation process. Further aspects of vulcanisation are dealt with in the next three chapters, namely, vulcanisation without sulphur (Ostromislenski), acceleration theory, and the physics of vulcanised rubber. Fillers, reinforcement, ageing and antioxidants follow. Then there is a chapter on the electrical behaviour of rubber by A. T. McPherson of the Bureau of Standards.

Next we come to latex: the properties of latex are discussed by W. A. Gibbons and P. D. Brass in a very satisfactory manner. The latter part of the chapter, covering the electrical charge on the particles, is a valuable review. Particularly interesting is the discussion on coagulation, including heat sensitisation, and the effects of hydration. In connection with the behaviour of the protein adsorption layer when dehydrating coagulants are used, it is interesting to remember that with some latices (for example, *Abiarana gutta* latex), water-miscible alcohols, ketones, and so on, are the only thorough coagulants. A few small points call for mention: the suggestion on p. 597 that the herring-bone tapping system still has a use on other than native-grown trees is surely incorrect, and so also is the inference that one must use glacial acetic acid for determining the dry rubber content. On p. 605 the amount of natural creaming which can occur, especially with preserved latex, appears to be somewhat understated. As regards the action of the creaming agent, the possibility of the increase in viscosity of the serum reducing Brownian movement and so promoting creaming has been overlooked.

Discussing the applications of latex in the next chapter Dr. Twiss and his co-workers point out that many of these were envisaged by the pioneers of the rubber industry, who were prevented from accomplishing anything by the absence of supplies of latex. It is clear from the account that follows that the position is very different to-day, and articles ranging from sponge rubber to "plastic flooring" are described. So far as can be seen, no novel applications have been disclosed.

An account of hard rubber (ebonite) comes next, and is followed by "Rubber Derivatives of Commercial Utility" by Dawson and Schidrowitz. There are not many accounts of this branch of the subject, nor of "Synthetic and Substitute Rubbers," which occupy the next chapter. These chapters are therefore particularly welcome. Gutta percha and reclaim are dealt with, and then comes a chapter on Practical Compounding by W. F. Russell, which is of interest as describing practical formulae and other details of manufacturing various rubber products.

Lastly, we come to the chapters of chief interest to the readers of THE ANALYST, namely, "Physical Testing and Specifications," by A. W. Carpenter, and "Chemical Analysis," by Dinsmore, Seeds and Rutledge. The latter chapter deals with raw and manufactured rubber, but not fully with latex. Both chapters give very detailed accounts of the subject and are also supplemented by full bibliographies;

they can be strongly recommended for all reference purposes in connection with rubber testing and analysis.

The book concludes with a chapter on the literature of rubber, and name and subject indexes.

As is stated in the preface, "the day is past when he who professedly devotes all of his attention to the chemistry of rubber can hope to be master even of his own small field." It appears likely, therefore, that joint work will become in future, even more than it is at present, the normal method of treatment. However, there is always some unevenness inherent in this system, so that it is to be hoped that giants will occasionally arise who will be able to deal with the whole subject broadly.

The "Chemistry and Technology of Rubber" is well printed and produced, but must nevertheless be regarded as expensive. W. H. STEVENS

APPLIED MYCOLOGY AND BACTERIOLOGY. By L. D. GALLOWAY and R. BURGESS. Pp. 186. Leonard Hill, Ltd. 1937. Price 10s.

This little book is intended to be an introduction to mycology and bacteriology and their application, and is written mainly for the benefit of workers in other scientific or industrial fields. It is divided into two parts: Part I deals with the description, classification and cultivation of bacteria and other micro-organisms and the technique required for their study, and Part II deals with their role in various industries, in hygiene and medicine, and in other applications; its scope is very comprehensive. In a volume of this size it is clearly impossible to go into much detail, and no attempt to do so has been made; the book is intended, rather, to give a bird's eye view of the whole scope of mycology and bacteriology, and the reader is directed in an ample and very helpful manner to books and other publications giving fuller information. To take only one example, under the heading Industrial Wastes one finds references to Papers 36 and 41 of the Department of Industrial and Scientific Research, and for dairy wastes, in particular, to recent papers by Parker, and Barritt and Muers. To each chapter a limited number of well-selected references is appended.

Part I contains chapters on Fungi, Bacteria, Apparatus and Sterilisation, Isolation and Examination of Micro-organisms, Culture Media and Stains, Metabolism of Micro-organisms and Control of Micro-organisms. There is a very clear and simple account of Bergey's system of classification, and a good description of methods of obtaining pure cultures is given. This part of the book is unencumbered with illustrations of sterilisers, microscopes, incubators, etc.

In Part II the following applications of bacteriology are dealt with:— (1) *Food Industries:* milk, cheese, butter and other dairy products, meat and fish, eggs, fruit and vegetable products, canning, cereals, sugar, and so forth. (2) *Fermentation Industries:* brewing, wine-making, fermented milk beverages, soy sauce, vinegar, distilled and industrial alcohol, glycerol, organic acids and solvents, bread-making and commercial yeast. (3) *Textile Industries:* both authors being specialists in these industries, one finds, as one would anticipate, a masterly, concise and very interesting account of the application of bacteriology to the manufacture and storage of cotton and woollen goods. (4) *Hygiene and Medicine:* Infection and

immunity, food and disease, air, water, sewage, industrial wastes. (5) *Agricultural Applications:* crop diseases, dissemination of plant diseases, control of plant diseases, soil bacteriology. (6) *Miscellaneous Applications:* timber decay, wood pulp and paper, rubber, leather, paints, moulds and arsenic compounds, tea, cocoa, indigo and tobacco, extraction of vegetable oils, use of micro-organisms for chemical analysis, future developments. These miscellaneous applications are of special interest, and one is surprised to find so many.

The book is very well written and, as the authors claim, free from technical jargon and consequently easy to read. It is admirably set out, the type and paper are good, and it is free from printer's errors. Both authors and publishers are to be congratulated upon its production. D. R. WOOD

SOIL SURVEY MANUAL. UNITED STATES DEPARTMENT OF AGRICULTURE. MISCELLANEOUS PUBLICATION NO. 274, WASHINGTON, D.C. By CHARLES E. KELLOGG. Pp. 136. 1937. Price 35 cents.

The manual is published for the use of soil surveyors engaged, or to be engaged, upon field work by the Bureau of Chemistry and Soils of the United States Department of Agriculture. The survey will provide maps primarily designed to show the various fundamental land types in an area, so that, for instance, a purchaser of land may be able to derive information as to the possibilities of plant growth and so on. A further use of the survey is apparently that of forming a basis of assessment for taxation purposes. The maps will also indicate those tracts of country where extensive agricultural work should not be undertaken on account of limited soil possibilities, and where profit from land would neither provide resources for the erection of schools for the education of settlers' children nor the means for the making of roads.

The publication indicates the system of enquiry undertaken during the last thirty-eight years, and is largely based on the ideas of hundreds of soil scientists who have worked in the field during that period. Full directions are given for almost every possible type of investigation that can be embodied in a survey, and as the manual contains no less than 136 pages the lot of a surveyor must indeed be difficult until familiarity with the contents is engendered by experience.

The manual would be useful to those desiring to become acquainted with instructions which would result in a very comprehensive soil survey.

F. W. F. ARNAUD

THE COSMETIC FORMULARY. HOW TO MAKE COSMETICS, PERFUMES, SOAPS, AND ALLIED PRODUCTS. H. BENNETT, F.A.I.C. Pp. xix. + 279 London: E. & F. N. Spon, Ltd. 1937. Price 18s. net.

This book contains some two thousand formulae for cosmetic and allied preparations, arranged in fifteen chapters, dealing with the various types of cosmetics, such as, for example, creams, lipsticks, eye preparations, hair preparations, depilatories and deodorants, face powders, dentifrices, and a sixteenth chapter giving formulae for miscellaneous preparations such as air purifiers, foot creams and ointments, remedies for corns and warts, and medicinal ointments.

As is very rightly stated in the preface, "a formula is useful as a starting

point, or to give one an idea," and this is probably the proper function of most published formulae. Used in this way, this volume should be extremely helpful to all engaged in the cosmetic industry, which is a rapidly growing one, and now, in the United States, "comes next to the food and clothing industries in volume of business done." It is rather surprising, however, that formulae which, according to the paper jacket on the cover, "have been sold for hundreds of pounds," should now be published in a book offered at a price which can only be regarded as very reasonable.

The author has been assisted in the compilation of the book by an editorial board of eleven colleagues, connected with various scientific institutions and industrial concerns, and the formulae appear mostly to be quite up to date, containing such comparatively modern ingredients as karaya and carob gums, sericin, glycol stearate and laurate, turtle oil, sulphonated fatty alcohols, trihydroxyethylamine stearate, carbitol, cellosolve acetate and sodium metaphosphate, so that it is a little incongruous to find "wood ashes" given as a material for soap-making. Also, under Soaps, *sulphonated* olive oil is wrongly given as a raw material for toilet soaps, when probably sulphur olive oil (*i.e.* oil extracted by carbon disulphide) is intended. The well-known irritating action of coconut and palm-kernel soaps on the skin is attributed by the author to the presence of fatty acids of low molecular weight, but no reason is suggested why this irritation should occur. Phenylenediamine appears as an alternative for 4-aminophenylglycine in one hair-dye formula, but this is an abstract of a German patent, and a warning is given that organic dyes "should only be applied by experts after testing the individual's reaction to the products to be used."

Throughout the book many substances are mentioned under proprietary or fancy names, and although at the end there is a table of "Common names of Chemical Products," this table is not very helpful, as some of the least-known substances are not included, and some of the information is inaccurate. Among the omissions may be mentioned glycosterin, deramin, stearoricinol, sodium *tribenzoate*, and among the synonyms given wrongly are sperm oil (whale oil), saccharin (glucoside), ground nut oil (aracha's oil), sulphur olive oil (olive oil foots), sodium bisulphite (sodium acid sulphate). Other tables at the end of the book include *p*H values of acids, bases, foods and biological materials, buffer systems, with approximate *p*H of maximum buffer capacity, and alcohol tables.

It is interesting, in conclusion, to note the author's statement that "more and more are cosmetic manufacturers beginning to realise the value of the chemist to the industry," and it is regrettable that the influence of the chemist is not more apparent in the advertisements of cosmetics which to-day are so prominent in all sections of the lay press.

W. H. SIMMONS.