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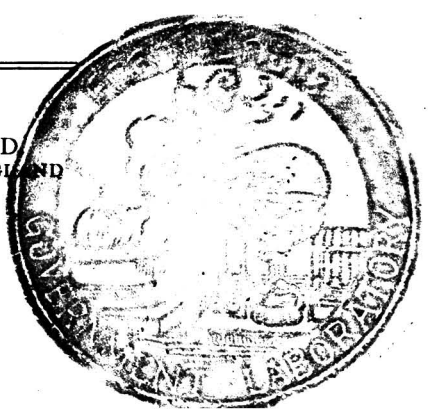

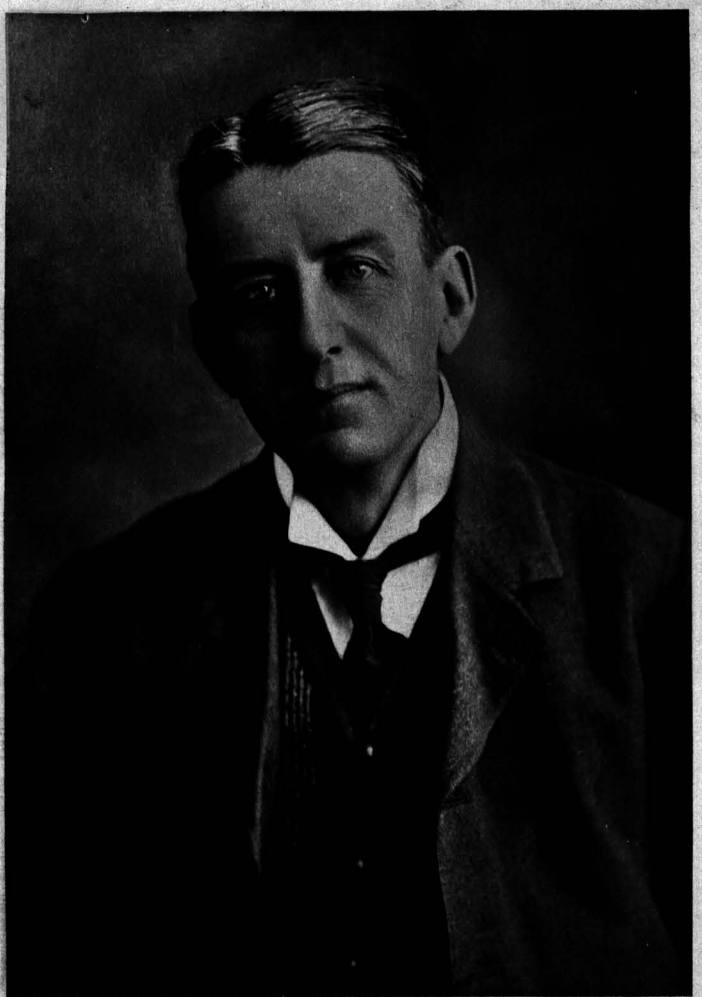

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Samuel Rideal

JANUARY, 1930. Vol. LV., No. 646.

THE ANALYST

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

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 4th, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of Ronald Gilbert Baskett, B.Sc., Hugh Charles Loudon Bloxam, F.I.C., Claud McClellan Bottomley, B.Sc., John Butler, B.Sc., F.I.C., Robert Ellison, A.M.C.T., George Noel Grinling, F.I.C., Albert Houlbrooke, M.Sc., A.I.C., Philip Henry Jones, F.I.C., Raymond Mallinder, Sydney Norman Herbert Stothart, B.Sc., Ph.D., A.I.C., Hubert Threadgold, B.Sc., A.I.C.

Certificates were read for the second time in favour of:—Noel Lionel Allport, A.I.C., James Gilbert Lunt, B.Sc., A.I.C., Fred Morris, F.I.C., Albert William Peters, Juda Hirsch Quastel, D.Sc., Ph.D., A.R.C.S., A.I.C., and Joseph Harold Totton, B.A., B.Sc., F.I.C.

The following were elected members of the Society:—Alfred George Avent, A.I.C., William Rhys Davies, F.I.C., Ernest Roadley Dovey, A.R.C.Sc., F.I.C., James Gray, F.I.C., James Henderson, B.Sc., A.I.C., Claude Alexander Scarlett, B.Sc., A.K.C., A.I.C., Percy Arthur William Self, B.Sc., F.I.C., Thomas Brooks Smith, B.Sc., A.R.C.S.

A lecture was given by Professor A. P. Laurie, M.A., D.Sc., on "The Methods of Examining Pictures," and the following papers were read:—"The Quantitative Analysis of Mixtures of Nickel and Cobalt," by S. Glasstone, D.Sc., and J. C. Speakman; and "The Changes with Age of the Hydrogen Ion Concentration of Egg White and Egg Yolk," by J. C. Baird, B.Sc., A.I.C., and J. H. Prentice, B.Sc., A.I.C.

NORTH OF ENGLAND SECTION.

A MEETING of the Section was held at Leeds on November 30th. There were 20 members present, and the Chairman (Mr. S. E. Melling) presided.

The following papers were read and discussed:—"A standard for Potted Meat," by C. H. Manley, M.A., F.I.C., and R. W. Sutton, B.Sc., F.I.C.; "Inquiry into some Problems connected with Milk," by C. J. H. Stock, B.Sc., F.I.C.; and "Further work on the Refractometer in Milk Analysis," by G. D. Elsdon, B.Sc., F.I.C., and J. R. Stubbs, M.Sc., F.I.C.

Obituary.

SAMUEL RIDEAL.

SAMUEL RIDEAL was the son of Mr. John Rideal, of Sydenham. He was born at Brixton in 1863. He obtained a Scholarship at Dulwich College, where he was a pupil from 1875 to 1878. He afterwards studied at the Royal School of Mines. While working at that institution he used to come to the meetings of the University College Chemical and Physical Society. In this way he got to know the pupils and teachers in the chemical and physical laboratories at University College.

Induced by the friendships he thus formed, he transferred his studies to University College, London. In 1883, during the Professorship of A. W. Williamson, he became Assistant in the Chemical Laboratory, and held this post for several years, including a short period during the Professorship of Sir William Ramsay, until, in 1889, he became Lecturer on Chemistry at St. George's Hospital Medical School. In 1884 he took the degree of Bachelor of Science at the University of London, with First Class Honours in Chemistry and a University Scholarship. In 1886 he obtained the Degree of Doctor of Science in the University of London, his subject being Inorganic Chemistry. Dr. Rideal was elected a Fellow of University College in 1888.

As a student he showed in a marked degree the power of setting forth his ideas with great clearness, both in speaking and in writing: a power which he retained throughout his successful career.

He married Lilla, daughter of the late Samuel Keightley, J.P., of Bangor, co. Down, by whom he had three sons and one daughter.

Rideal was a man who had the courage to hold his own opinions in spite of opposition, as the writer discovered in a delightful wandering with him and the late Dr. Richard Plimpton in 1884 in the Yellowstone Park, which was then hardly known and to a large extent unmapped.

While still at University College, Rideal published, with Arthur G. Green, "A New Volumetric Method for the Estimation of Nitrous Acid," depending on

the conversion of an acid solution of aniline into diazobenzene (*Chem. News*, 1884, **49**, 173–174). This method has been of much service in analytical work. He also published "Delicacy of some Tests for Antimony, Arsenic and Tin," in which two wires of different metals, twisted together, are placed in acid solutions of the salts (*Chem. News*, 1885, **51**, 292).

In the *Berichte* of the German Chemical Society (*Ber.*, 1886, **19**, 589–591) he turned his attention to "Isodimorphism," as shown in the specific volumes of arsenic and antimony trioxides in their octahedral and prismatic forms. In the same year he read before the Chemical Society a "Note on the Action of Ammonia on Chromyl dichloride" (*Chem. Soc. Trans.*, 1886, 367–369). This was followed by a paper on the "Action of Ammonia on Tungsten Compounds" (*Chem. Soc. Trans.*, 1889, 41–45), dealing with the formation of tungsten nitride and derivatives.

While at St. George's Hospital Medical School he published "Organic Boron Compounds," in which the action of the chloride, bromide and fluoride of boron on ammonia and on organic bases is dealt with (*Ber.*, 1889, **22**, 992). A little later he published, with S. G. Rosenbaum, "Estimation of Chromium in Chrome Ore and Ferrochromium, using Sodium Peroxide" (*J. Soc. Chem. Ind.*, 1895, **14**, 1017; 1896, **15**, 155–158; *Chem. News*, 1896, **73**, 1–2).

In 1889 the first of his books was published. This was "Practical Organic Chemistry for Medical Students," and had a second edition in 1898. The book was written primarily to help his students at St. George's Hospital Medical School in their laboratory work, but was found useful by other teachers. Dr. Rideal contributed the articles "Fermentation," "Paraffin," "Petroleum" and "Tannin" to the new edition of *Watts's Dictionary of Chemistry*, which came out in 1886–1890.

About this time, Rideal became Public Analyst for Chelsea, and set up a consulting practice in Westminster. He took an active interest in this work for thirty-five years. He was also, for a short time, Public Analyst for Lewisham. Henceforth he devoted himself more particularly to questions relating to sanitation, sewage purification and water supply. Among the more important sewage cases in which he was concerned may be mentioned those at Sheffield, Poole, Southend, Dublin and Southampton.

It would not be possible to give a complete list of the 101 contributions that Dr. Rideal made to science, but some of the more important may be mentioned. He often took part in discussions at the meetings of the societies of which he was a member, his observations being usually drawn from his own experience.

Of his books, "An Introduction to the Study of Disinfection and Disinfectants," published in 1895 (Chas. Griffin & Co., 292 pp.), had later editions in 1898 and 1904; "Water and its Purification," published in 1897, had a second edition in 1901; "Sewage and the Bacterial Purification of Sewage," published in 1900, had new editions in 1901 and 1906. The third edition, published by the Sanitary Publishing Co., contains 348 pages and 58 illustrations. He also published in 1914, in conjunction with his son, Dr. Eric K. Rideal, "Public Water Supplies."

"The Carbohydrates and Alcohol" (219 pp.), by S. Rideal and associates, appeared in 1920 in the Industrial Chemistry Series published by Ballière, Tindall & Cox.

The Rideal-Walker method for determining the antiseptic value of disinfectants, notwithstanding its well-recognised limitations, is still widely used.

In 1893 Rideal published a paper on "Sulphuric Acid Hydrolysis of Butter Fats" (ANALYST, **18**, 165), and in 1894, in conjunction with H. J. Bult, an article on "Sodium Peroxide in Water Analysis" (*Chem. News*, **68**, 190–191), showing that part only of the organic matter is attacked. An important paper on the minimum amount of boric acid and of formaldehyde required as milk preservatives appeared in 1899 (S. Rideal and A. G. R. Foulerton, *Public Health*, **11**, 554).

In conjunction with C. G. Stewart he published an article on the "Estimation of Proteids by Chlorine" (ANALYST, 1897, **22**, 228), in which they discuss the precipitation of gelatin from meat extracts by a dilute solution of chlorine.

In 1901, Rideal and C. G. Stewart published (ANALYST, **26**, 141) an important paper on the "Estimation of Dissolved Oxygen in Waters in the presence of Nitrites and of Organic Matter" by the manganous chloride method.

Rideal's work on the use of electrolytic chlorine in sewage purification and deodorisation must also be mentioned (*J. Roy. Sanit. Inst.*, 1905, **26**, 378–406; *J. Soc. Chem. Ind.*, 1909, 215), as well as that on the use of ozone as a sterilising agent (*J. Soc. Chem. Ind.*, 1909, 215). Indeed, his investigations had great influence on the design of modern plants for water and sewage purification, on which he was an acknowledged expert.

At the meeting of the British Association at Glasgow in 1901 he read a paper on "Sulphuric Acid as a Typhoid Disinfectant," especially for the sterilisation of drainage water in typhoid epidemics. But he did not by any means confine his attention to questions of sanitation. Thus, in conjunction with L. H. D. Acland, he published, in 1913, a research upon the oils from the seeds of *Manihot ceara* (ceara rubber) and *Funtumia elastica*, comparing the properties of these oils with those of linseed and Hevea (ANALYST, 1913, **38**, 259). In 1900 he published a book on "Glue and Glue-testing," and in 1906, in conjunction with H. G. Harrison, a paper on the Polenske method for detecting coconut oil in butter (ANALYST, 1906, **31**, 254). These examples will show that original investigations carried out in Dr. Rideal's laboratory covered a wide range of subjects, though they centred, for the most part, about problems in sanitation.

He had the power of inspiring confidence and affection in his staff, two of whom, Messrs. Stewart and Orchard, were with him all their lives.

Dr. Rideal was an active member of the Society of Public Analysts, twice serving on the Council, being Vice-President in 1899–1900, and President in 1918–19. He was elected a Fellow of the Institute of Chemistry in 1878, and served on its Council from 1899–1902. He acted as Examiner to the Conjoint Board of the Royal Colleges of Physicians and Surgeons. In 1902 he gave the Cantor Lectures on "Water Purification" to the Society of Arts (*J. Soc. Arts*, 1902, **50**, 717, 729, 741, 755). In the same year he became President of the Association of Sewage

Works Managers. He gave evidence before the Royal Commission on Sewage Disposal and at a number of other Government inquiries.

His large circle of friends have been very anxious of late years about his health. A visit to South Africa failed to restore him, for he died suddenly at Hartley, in Southern Rhodesia, on November 13 last, at the age of 66.

H. F. MORLEY.

The Grouping of Fatty Oils, with Special Reference to Olive Oil.

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

(*Read at the Meeting, November 6th,* 1929.)

IN the course of an investigation, with the object of distinguishing olive oil from other oils, and, in particular, from tea-seed oil, we were led to study the degree of unsaturation of the unsaponifiable matter of various oils.

HALOGEN ABSORPTION OF STEROLS.—In connection with the halogen absorption of sterols, Lewkowitsch ("Chemical Technology of Oils, Fats and Waxes," Vol. I, 6th edn., pp. 272, 273, 282, 617) and others state that the absorption of halogen by pure sterols from Wijs iodine monochloride solution is irregular, and gives results which are much higher than is required by theory. Satisfactory figures, however, are obtained by the Hübl method. Thus, Matthes and Heintz (*Arch, Pharm.*, 1909, **247**, 161) found for sitosterol a value of 62·8 (theory 65·5); Lewkowitsch (*ibid.*) found for cholesterol values ranging from 67 to 68 (theory 65·5). The Wijs method yields results for these sterols lying between 135 and 145. It, therefore, appears that, to obtain satisfactory absorption, a milder halogenating agent than iodine monochloride must be employed. Dam (*Biochem. Z.*, 1924, **152**, 101; 1925, **158**, 76) has reported some success in determining the iodine values of cholesterol and coprosterol by the Hanus method, but recommends, in preference, the use of the pyridine sulphate bromide reagent described by Rosenmund and Kuhnhenn (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154). This quick and simple method makes use of a very stable halogenating agent, and has been used by Smedley Maclean (*Biochem. J.*, 1928, **22**, 23), and by Copping (*Biochem. J.*, 1928, **22**, 1142) for other sterols with satisfactory results in all cases, except that of ergosterol.

CRUDE UNSAPONIFIABLE MATTER OF OILS.—These researches upon halogenation have not, as far as we have been able to ascertain, been applied to the crude unsaponifiable matter of oils in general. We have found that when the Wijs and Hübl methods are used with crude unsaponifiable matter, the Wijs method gives erratic results, while the Hübl method gives lower figures which are fairly constant. We have found, however, that the method of Rosenmund and

Kuhnhenn is simpler to operate than that of Hübl, and gives in a few minutes results which are at least as accurate and satisfactory. For these reasons, we have applied it to the unsaponifiable matter of a large number of oils in the following manner:—

(i) *Preparation of Unsaponifiable Matter.*—From 2 to 2·5 grms. of the oil are saponified by boiling under a reflux condenser with 25 c.c. $N/2$ alcoholic potash. The solution is titrated with $N/2$ HCl, using phenolphthalein as indicator. Five c.c. of $N/2$ NaOH are added, and the solution is extracted three times (or more in the case of certain fish oils) with 30 to 40 c.c. of petroleum spirit. The extracts are combined, washed with 20 c.c. of $N/20$ NaOH and then with 20 c.c. of water, and filtered into a weighed flask, the petroleum spirit is evaporated off, and the contents dried and weighed. In general this procedure will yield a quantity varying between 0·01 and 0·04 grm. of unsaponifiable matter free from soap and fatty acids.

(ii) *Determination of Iodine Value of Unsaponifiable Matter.*—Pyridine sulphate bromide reagent $N/10$ is made as follows:—Two solutions are prepared, the first by mixing 8 grms. of bromine with 20 c.c. of glacial acetic acid, and the second by adding, gradually, 10 grms. of concentrated sulphuric acid to a mixture of 8 grms. of pyridine and 20 c.c. of glacial acetic acid, the mixture being cooled during the addition. The two solutions are mixed and cooled and the whole is diluted to 1 litre with glacial acetic acid.

METHOD.—The unsaponifiable matter is dissolved in 5 c.c. of chloroform and a quantity of the pyridine sulphate bromide reagent sufficient to leave an excess of unabsorbed halogen approximately equal to the amount absorbed is added (*cf.* Wijs iodine values); usually this will be 10 c.c. of the reagent. The mixture is allowed to stand in the dark for five minutes; 5 c.c. of 10 per cent. potassium iodide solution are added, together with 40 c.c. of water, and the iodine liberated is titrated with $N/20$ sodium thiosulphate solution. A blank experiment is carried out in the same manner with the reagents. The amount of halogen absorbed is calculated in terms of iodine as a percentage of the weight of unsaponifiable matter taken, in the same manner as for the Wijs iodine value. It is essential, in conducting this test, that the method prescribed for obtaining the unsaponifiable matter be strictly adhered to, in order that this substance may be prepared in the necessary state of purity.

We find that duplicate determinations, on a given sample, give results that do not vary by more than about 3 per cent. of the observed figure, at the most, and, in view of the difficulty usually experienced of obtaining larger quantities of unsaponifiable matter uncontaminated by soap or other impurities, we believe that this degree of accuracy is the greatest that can be obtained at the present time.

DISCUSSION OF RESULTS.—As stated above, we have applied this test to a large number of the most commonly-occurring oils and fats, and we find that, with the one exception of soya bean oil, dealt with later, each gives an iodine value lying in one of four narrow ranges, shown in the table of groups (Table I).

The natural oils and fats are thus split into four groups, each of which contains not more than two sub-groups. In each group occur oils of similar origin:

Group 1.—Iodine value 64 to 70. This group contains the animal fats and a few vegetable fats (the coconut group).

Group 2.—Iodine value 90 to 96. This contains the fish and marine animal oils and cocoa-butter.

Group 3.—Iodine value 117 to 124. This contains the vegetable oils and fats.

Group 4.—Iodine value 197 to 206. This contains olive oil only.

The grouping of the oils which we have so far examined is given in Table I.

TABLE I.

IODINE VALUE OF THE UNSAPONIFIABLE MATTER OF OILS.

Group 1. Iodine value 64 to 70.		*Group* 2. Iodine value 90 to 96.		*Group* 3.	*Group* 4.
Animal oils and fats.	Vegetable oils.	Fish and marine animal oils.[1]	Vegetable oils.	Vegetable oils and fats.	Vegetable oil.
Beef	Kernel oils of *Palmae*:	Cod liver	Cocoa-butter	Almond	Olive
Butter-fat		Herring		Arachis	
Ghee		Seal		Borneo tallow	
Lard	Coconut	Sardine		[2]Cotton	
	Palm kernel	Whale		Dhupa	
	Babassu			Grape seed	
				Linseed	
				Maize	
				Palm	
				Rape	
				Rubber-seed	
				Sesame	
				[2]Soya	
				Sunflower	
				Tea-seed	
				Tung	

[1] Containing less than 2 per cent. unsaponifiable matter.

[2] After refining with alkali and bleaching with fuller's earth and charcoal.

It will be noticed that the iodine value of two of the four groups of unsaponifiable matter is approximately the same as that of certain sterols. This suggests that the unsaponifiable matter consists mainly of sterol—a suggestion that we have confirmed by experiments made upon larger quantities of unsaponifiable matter extracted from various oils. In this connection, we may mention that we have found a relation to exist between the proportion of sterols and unsaponifiable matter, on the one hand, and the iodine value of the oil, on the other. Thus the oils of higher iodine value contain, in general, more unsaponifiable matter and a larger proportion of sterols than do those of lower iodine value.

Except in the case of soya bean oil, the iodine value of the unsaponifiable fraction is not altered by those processes of refining and bleaching of oil commonly

in use which do not involve the heating of the oil to high temperatures; the application, however, of temperatures of 200° C. and over for any length of time causes a reduction in the iodine value to a degree depending on the nature of the oil. We find, however, that if this treatment be prolonged a limit to the reduction of the iodine value is reached. In this state olive oil still remains in a class by itself, the iodine value of all vegetable oils being reduced proportionally. We are at present investigating the most suitable means of extending the test to include heat-treated oils, so that they may be recognised by a less elaborate method than we now employ.

Investigations are also being conducted in connection with the refractive index of the unsaponifiable matter, with the result that preliminary indications show a likelihood of great utility from this figure, as it does not alter appreciably after heat-treatment of the oil.

The refractive index of the unsaponifiable matter of olive and tea-seed oils is markedly different, and were it not for the more elaborate manipulation necessary to prepare the larger quantities of sufficiently-pure unsaponifiable matter, the refractive index might well supersede the iodine value for the purpose of distinguishing between olive and tea-seed oils.

Soya Bean Oil.—The only oil that we have so far discovered which does not, in its crude state, give figures lying definitely in one of the four groups, is soya bean oil. The crude oil contains a proportion of unsaponifiable matter, varying between 0·75 per cent. and about 1·5 per cent., the iodine value of which varies from about 75 to 120. This variation appears to be caused by the presence in the oil of a varying amount of unsaponifiable matter other than sterol, but associated with the colouring matter of the oil. We find that the refining of the oil with alkali, and bleaching with fuller's earth and charcoal, reduce the proportion of unsaponifiable matter to a minimum amount lying between 0·75 and 0·90 per cent., whilst the iodine value rises to a value between 117 and 124; that is to say, the oil takes its place in Group 3, the group containing the liquid vegetable oils.

Olive Oil.—The high value obtained for olive oil, and the great difference between this and the much lower values of all the oils that are used as adulterants, render this method extremely useful in the detection of adulteration of olive oil. Since the adulterants contain approximately the same proportion of unsaponifiable matter as olive oil, it follows that the addition of as little as 10 per cent. of any other oil to olive oil will bring this iodine value outside the limits for the pure oil, and the reduction will be proportional to the amount of the adulterant present.

Rancid Oils.—The production of rancidity in oils is accompanied by a reduction of the iodine value of the unsaponifiable matter; so that, while an edible beef tallow gives a value of about 66, rancid tallows have been found to give values of from 45 to 52, and, in one case, 31. The connection between the degree of rancidity and this iodine value has yet to be worked out, but preliminary experiments show that such a connection probably exists.

CONCLUSIONS.—(i) That a determination of the iodine value in the manner described, upon the crude unsaponifiable matter, obtained in the way we have specified, enables fatty oils to be divided into four main groups ;

(ii) That olive oil lies in a group alone, and is thus chemically distinguishable from other oils, and, in particular, from tea-seed oil, in a manner hitherto impossible.

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LONDON, S.W.3.

DISCUSSION.

The PRESIDENT remarked that this was a remarkable investigation, throwing light on a very difficult problem. He felt that the authors had produced a method of analysis, and some means of settling the special question of olive oil, on entirely new lines. It was most remarkable and fortunate that olive oil stood in a position by itself, and he prophesied that this method would be very largely applied. He had noticed that the authors laid particular stress on the necessity for using his exact method for determining unsaponifiable matter. More than one paper had been read before the Society on this subject, and he gathered that this was an extremely satisfactory way of determining unsaponifiable matter. He then referred to the error of 3 per cent. mentioned by Mr. Bolton; was this the variation between one olive oil and another; or was it experimental? (Mr. Bolton here informed the President that it was the maximum error of experiment.) Regarding the effect of heat and the reducing of all oils to the same denomination, if one were confronted with an unknown oil, would Mr. Bolton advise the analyst to heat it at 200° C. and see its effect? Also was heating carried out in the absence of air or not?

Mr. T. MACARA thought that Mr. Bolton was to be congratulated on evolving something entirely novel, which seemed to be a very simple test. Even if one were dealing with heated oil, it seemed that the only possible effect would be to bring olive oil into the tea seed oil group, which was better than bringing tea seed oil into the olive oil group. Another interesting point in the table, he thought, was that it was the first time that he had seen cocoa butter differentiated from Borneo tallow, *i.e.* chemically. He asked if the cocoa butter had been purified in any way. Finally, Mr. Macara suggested that the test should be called the Bolton–Williams Test.

Mr. H. JEPHCOTT asked whether Mr. Bolton had compared his results on the unsaponifiable matter of the various oils with the examination of the absorption spectra of similar oils recently carried out at Liverpool University. He thought such a comparison might afford an intersting cross check on the iodine values. He would like to suggest that Mr. Bolton gave some further particulars of the method of separating unsaponifiable matter, since there was always a possibility that this had been incompletely extracted.

Mr. N. D. SYLVESTER said that he would like to add his congratulations. It was the first occasion on which he had met what appeared to be a reliable method for detecting Borneo tallow in cocoa butter, and he thought that the test could probably be used quantitatively. Mr. Bolton had not mentioned the effect of hydrogenation on the unsaponifiable matter. Although the vegetable oils fell into the same group, it was possible that the hydrogenated products might not, and it would be interesting if the test could be further applied. He also enquired

whether Mr. Bolton had determined the iodine value of the unsaponifiable matter for the common adulterants of almond oil.

Dr. C. A. MITCHELL, after congratulating the authors on their ingenious method, said that the fact that the Wijs reagent gave abnormal results with the sterols, whereas the pyridine sulphate bromide reagent gave normal figures, was significant, and he mentioned that Margosches had also claimed that his rapid iodine method was applicable, with certain modifications, to these compounds. He asked whether the authors had determined the thiocyanogen value of the unsaponifiable matter, and suggested that the method might be usefully extended along the lines of differential absorption.

Mr. R. F. INNES asked Mr. Bolton if there was any connection between the four groups and the formation of vitamin *D* on exposure to ultra-violet light. It seemed that one would not expect to get vitamin *D* formed by the members of Group I, but possibly from Groups III and IV.

Mr. A. L. BACHARACH referred to the proved fact that it was very difficult to free the unsaponifiable matter of oils from traces of soap or fatty acids. He thought that it was conceivable that Mr. Bolton's unsaponifiable matter might be slightly contaminated in this way.

Mr. K. A. WILLIAMS, in thanking the members for their kind reception of the paper, said that he thought that the experimental error of 3 per cent. was accounted for almost entirely by the difficulty of weighing accurately a small quantity of material in a comparatively large flask. An error of one milligram in such weighing would be sufficient to account for almost the whole of the observed experimental error, while the error involved in the titration was very much smaller.

He regarded the method as empirical only in so far as it was necessary to follow a standard method of extracting the unsaponifiable matter in order to obtain a pure specimen. The determination of the iodine value was no more empirical than was the Wijs method; it was, in fact, strictly comparable with that method. He thought that any method which was known to yield the unsaponifiable matter in a pure state was suitable, but he recommended the method which the authors described not only as being suitable, but as the one used in obtaining the results quoted in the paper.

He had found that with most of the oils to which the test had been applied the unsaponifiable matter was completely removed in three extractions, and was obtained free from soap and fatty acids if the soap solution was rendered alkaline, to the extent specified, before extraction. Further, the iodine values of the unsaponifiable matter removed in the first and second extractions were the same within the limits of experimental error. The question of the reduction of the value of a given oil through heat treatment was one upon which the authors had been working; they had been experimenting with certain methods of treating oils with the object of bringing the iodine value of the unsaponifiable matter down to the limiting values observed in heat-treated oils. While one of these methods seemed to be satisfactory it required further trial before it could be communicated to the Society.

Hydrogenation of an oil reduced this iodine value to a limiting value in the same way as did other forms of heat treatment. In this case, however, some factor other than temperature was involved, since the same reduction of the value could be brought about by operating at 100° C.

It was possible that the value for cocoa butter would be reduced to 65 if the oil were refined and bleached, in the same way that the value for soya bean oil was raised to 120. Crude cocoa butter, however, differed from crude soya bean oil in that, while the values for the latter ranged from 75 to 120, those yielded by cocoa butter seemed to be a constant, the values of the dozen or so samples which

the authors had tested lying between 90 and 96. Consequently he inclined to the view that refining and bleaching would not alter the observed value for cocoa butter; the matter could easily be settled by experiment.

Finally, as regards Dr. Mitchell's question about the effect of various halogenating agents upon the unsaponifiable matter of oils, the authors had shown that the Wijs reagent was so reactive that it gave erratic and abnormally high values; bromine, of course, was even fiercer in its action, and it was not until the authors had investigated the milder pyridine sulphate bromide that they had found a reagent sufficiently delicate to use. They had made a few experiments with the thiocyanogen reagent, obtaining, in the case of olive oil, figures somewhat lower than by the method described in the paper. Their experiments with the thiocyanogen method had not yet been carried far enough to be reported.

At the conclusion of this discussion the PRESIDENT stated that it was the feeling of the entire meeting that the test should be called "the Bolton–Williams test."

A Standard for Potted Meat.

BY C. H. MANLEY, M.A., F.I.C., AND R. W. SUTTON, B.Sc., F.I.C.

(*Read at the Meeting of the Northern Section on November* 30, 1929.)

BY "potted meat" is generally understood a cooked meat seasoned and contained in a finely divided state in a pot or dish. It is therefore distinct from a meat paste, the name of which implies that some such ingredient as starch has been added to the meat to enable even spreading upon bread and butter. Our experience is that, whilst the majority of potted meats offered for sale contain no starch, an appreciable number contain starch in some form or other to an extent not usually exceeding 10 per cent. In Leeds 20 per cent. of the potted meats (5 out of 25) submitted by the food inspectors in the course of a year contained starch in amounts varying from 1·0 to 7·5 per cent., whilst in another city 36 per cent. (9 out of 25), similarly submitted in six months, contained starch varying from 1·5 to 11·0 per cent. In none of these cases was any action taken by the local authority. Bell's "Sale of Food and Drugs" (1927) states:—"Starch, usually in the form of rice flour and bread, is sometimes found in substantial quantities in potted meats. If the quantity be excessive this may be considered as an adulteration." No instances are given in Bell of any cases in which legal proceedings have been instituted, nor do the food journals contain any such records.

A few analyses are quoted by Mitchell in *Flesh Foods* (p. 119), and König (*Die Menschlichen Nahr. u. Genussm.*, Vol. I (1903), p. 97, and Vol. II (1904), p. 522) gives analyses of a number of English preparations. There are also some analytical data by Ellis Richards in a report on canned foods to the Local Government Board by MacFadden in 1908, but there do not seem to be any recent figures available in the literature.

In his Report MacFadden observes: "Starch, usually in form of rice flour, is sometimes present in such amounts in some kinds of potted meats that these may be thought to constitute a fraud on the consumer, notwithstanding their cheap price. The matter seems worth the attention of better-class manufacturers, with the view to arriving at a reasonable maximum limit of permissible starchy matter in specified canned foods of this class."

The water content is subject to considerable variation. In the Leeds samples it varied from 55 to 80 per cent., and it is not unusual to find that some of the samples which are free from starch contain the highest proportion of water, and *vice versa*. For example, a sample with 7·5 per cent. of starch contained only 57·2 per cent. of water, whilst two samples free from starch contained 79·2 and 79·7 per cent. of water, respectively.

When it is realised that a potted meat containing 77 per cent. of water has been known to sell at 3s. 4d. per lb., it should be obvious that it is time that some standard for potted meat should be recognised.

The subjoined table contains the results of the analyses of 22 potted meats sold in Leeds. In several cases detailed analyses have been made, whilst in others determinations only of the meat solids and water are returned.

The total solids and water were determined by drying 1–2 grms. of the sample in a flat dish containing a short glass rod with a flattened end; the fat, by extracting the powdered dry solids with petroleum spirit (b.pt. 40–60° C.), and determining both by loss in weight and by direct weighing in a flask after evaporating off the solvent; the mineral matter, by ashing the residue from the fat extraction; the proteins by the Kjeldahl method on 1–2 grms. of the sample; and the starch, after hydrolysis with dilute hydrochloric acid, gravimetrically by means of Fehling's solution.

No reduction of Fehling's solution was effected by samples in which iodine had indicated absence of starch. The method of Stokes (ANALYST, **1919, 44,** 128) involving the use of alcoholic sodium hydroxide, was also tried, with satisfactory and similar results.

The average water content of the 17 samples free from starch was 68·6 per cent., and that of the 5 samples containing starch 68·30 per cent. A home-made potted meat contained 65·60 per cent. In this case the product was prepared from prime steak which was cut into small pieces, covered with water in a jar, and heated by immersion in a pan of boiling water. When cooked, the meat was strained from the gravy formed, and minced, after which some of the gravy, along with a small proportion of mace, pepper and salt, was mixed with the minced meat, the product being then placed in a dish and covered with melted butter. The excessive amounts of water found in some potted meats are, doubtless, introduced with the gravy, and with proper care are avoidable. An alternative method of manufacture consists in omitting the addition of gravy, and mincing meat already roasted or boiled, and adding spices only. This type of potted meat will obviously have a lower water content than one made by the first method.

As a result of the foregoing considerations we submit that a reasonable standard for potted meat is one which limits the water content to a maximum of 70 per cent. and excludes the presence of starch.

POTTED MEATS CONTAINING NO STARCH.

	Water. Per Cent.	Total solids. Per Cent.	Fat. Per Cent.	Proteins. Per Cent.	Ash. Per Cent.
1	67·3	32·7	—	—	—
2	58·5	41·5	—	—	—
3	70·8	29·2	—	—	—
4	72·3	27·7	6·7	19·6	1·4
5	71·1	28·9	8·9	17·8	2·2
6	67·7	32·3	12·8	16·8	2·7
7	55·3	44·7	22·9	20·5	1·3
8	61·1	38·9	21·0	16·6	1·3
9	79·2	20·8	4·6	14·8	1·4
10	79·7	20·3	2·6	15·7	2·0
11	74·5	25·5	—	—	—
12	69·4	30·6	—	—	—
13	59·1	40·9	—	—	—
14	64·2	35·8	—	—	—
15	77·3	22·7	—	—	—
16	66·6	33·4	—	—	—
17	72·0	28·0	—	—	—
Average	68·6	31·4			

POTTED MEATS CONTAINING STARCH.

	Water. Per Cent.	Total solids. Per Cent.	Fat. Per Cent.	Proteins. Per Cent.	Ash. Per Cent.	Starch. Per Cent.
1	68·7	31·3	10·6	12·6	2·1	6·0
2	57·2	42·8	16·2	17·1	2·0	7·5
3	71·2	28·8	15·0	10·9	1·9	1·0
4	68·2	31·8	10·5	14·6	1·7	5·0
5	76·2	23·8	7·5	9·4	2·7	4·2
Average	68·3	31·7				

The Heat Resistance Curve: A New Bacteriological Test for Pasteurised Food.

By CUTHBERT DUKES, M.D., M.Sc., D.P.H.

(*Read at the Meeting, November* 6, 1929.)

The Heat Resistance Curve Test is designed to answer the question: Has a sample of food been pasteurised, and, if so, at what temperature? The principle of the test is a simple one, and the technique is within the scope of anyone trained in elementary bacteriology. The test has proved of value in determining whether or not milk and cheese have been pasteurised, and it is likely to have other applications in the analysis of food.

The idea on which the test is based is that if food has been pasteurised, at say 60° C., then a re-heating of the food to any temperature less than 60° C. will not greatly reduce the number of bacteria, whereas heating above the pasteurising temperature of 60° C. will progressively reduce the number of bacteria per grm. or per c.c. This is due to the fact that bacteria living in pasteurised food have already withstood, and can again withstand, a temperature of 60° C. The mixed bacterial population of unpasteurised food, on the other hand, is reduced progressively as the temperature is raised from 50 to 60° C. and onwards. In short, pasteurised food differs from unpasteurised in that subsequent heating causes a large reduction in the number of bacteria, only when temperatures higher than the pasteurising temperature are reached, whereas in unpasteurised food the bacteria are reduced progressively and uninterruptedly as the temperature is raised.

Liquid food requires no preliminary treatment other than thorough shaking to ensure fair sampling. Solid food is cut with a sterile knife, and one grm. is weighed and ground up with sterile water to make a 10 per cent. or 1 per cent. suspension, according to whether the food is known to contain few or many bacteria. About 5 c.c. of the liquid to be examined are poured into each of five sterile test tubes, which are marked A1, B1, C1, D1, E1, and F1. The tubes B1, C1, D1, E1, and F1 are placed in water-baths adjusted at 50° 55°, 60°, 65°, and 70° C., respectively, for half-an-hour. Meanwhile tube A1 stands on the bench at room temperature. This treatment provides six fractions of the food, one of which has not been heated, whilst five have been heated between 50° and 70° C.

A quantitative bacteriological examination by the agar plate method is now employed for each of the tubes A1, B1, C1, D1, E1, and F1. Thus, 1 c.c. from A1 is transferred with a sterile pipette to a tube containing 9 c.c. of sterile water; this is marked A2, and provides a dilution of 1 in 10 of the liquid under examination.

After thorough mixing, 1 c.c. from A2 is transferred to another tube containing 9 c.c. of sterile water. This is marked A3, and provides a dilution of 1 in 100 of the liquid being examined. Similar dilutions are made from tubes B1, C1, D1, E1, and F1, a separate sterile pipette being used for each series.

Meanwhile the 18 tubes of nutrient agar have been melted in boiling water and cooled to 50° C. One c.c. from each of the eighteen test tubes is added to a tube of melted agar and poured into a Petri dish at once. The Petri dishes are labelled to correspond with the test tubes from which they were charged, *e.g.* A1, A2, A3, B1, B2, B3, etc. After solidification of the agar the plates are incubated at 37° C. On the third day the colonies visible to the unaided eye on each plate are counted.

In calculating the number of bacteria per c.c. or per grm. the average of the three plates 1, 2 and 3 is taken, but accurate results can only be obtained from plates which show less than 2000 colonies. If, for instance, plate A1 contains 320 colonies; plate A2, 43 colonies; and A3, 4 colonies, the number of bacteria per c.c. in A1 is recorded as the average of 320,430 and 400=383. But if A1 contained more than 2000 colonies the result is based only on the average counts of A2 and A3.

When an examination is made of an unpasteurised food plentifully stocked with bacteria, the heat resistance test reveals a great reduction in the number of surviving bacteria as the scale is ascended from 50° to 70° C. For example, a test was made from unpasteurised fresh Cheddar cheese, and this showed the following figures:—

Unheated fraction ..	more than 10 million bacteria per grm. of cheese
Heated at 50° C.	300,000 bacteria per grm.
,, ,, 55° C.	25,000 ,, ,, ,,
,, ,, 60° C.	800 ,, ,, ,,
,, ,, 65° C.	200 ,, ,, ,,
,, ,, 70° C.	less than 50.

For purposes of comparison it is useful to record the result as the effect of heat on a bacterial population of 1,000, a calculation which gives in this case the following figures:

Unheated fraction	1,000
Heated at 50° C.	30
,, ,, 55° C.	2·5
,, ,, 60° C.	0·08
,, ,, 65° C.	0·02
,, ,, 70° C.	0·005

When these figures are plotted out as a graph (Fig. 1), a characteristic curve is obtained, the steep decline of which is typical of unheated food.

When the test was applied to a pasteurised Cheddar cheese the figures obtained were as follows:

Unheated fraction	500 bacteria per grm.
Heated at 50° C. ..	500 ,, ,, ,,
,, ,, 55° C. ..	725 ,, ,, ,,
,, ,, 60° C. ..	1,050 ,, ,, ,,
,, ,, 65° C. ..	800 ,, ,, ,,
,, ,, 70° C. ..	350 ,, ,, ,,

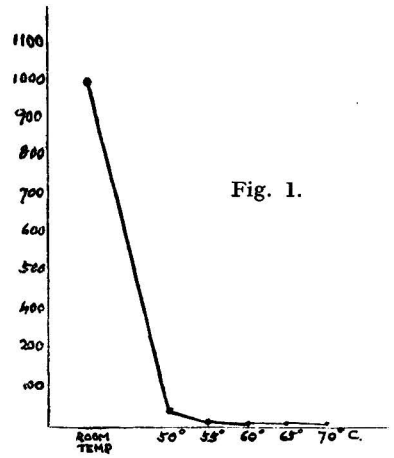


Fig. 1.

Calculated for a population of 1,000 the figures are:

Unheated fraction ..	1,000
Heated at 50° C.	1,000
,, ,, 55° C.	1,450
,, ,, 60° C.	2,100
,, ,, 65° C.	1,600
,, ,, 70° C.	700

The graph of these figures (Fig. 2) shows no sharp decline until the pasteurising temperature (60° C.) has been exceeded. Until that point is reached there may be actually an increase in the bacterial count, due presumably to a proliferation of the heat-resisting bacteria which have survived pasteurisation, and which increase in numbers as the test fractions are re-heated. Such a rise in the bacterial count in pasteurised food is not an invariable experience in the heat resistance test, but it has occurred in the majority of tests made. The important point which distinguishes the unpasteurised from the pasteurised cheese is that in the former the reduction in numbers is immediate and progressive, whereas this immediate and continuous reduction does not take place in pasteurised food.

The application of the test may be illustrated also by a record of two tests carried out on milk—one on unpasteurised Grade A (Tuberculin tested) milk, and the other on the same milk previously pasteurised in the laboratory at 60° C.

Unpasteurised Grade A Tuberculin Tested Milk.

		Per 1000
Unheated fraction ..	250,000 bacteria per c.c.	1,000
Heated at 50° C.	120,000 ,, ,, ,,	480
,, ,, 55° C.	80,000 ,, ,, ,,	320
,, ,, 60° C.	45,000 ,, ,, ,,	180
,, ,, 65° C.	7,500 ,, ,, ,,	30
,, ,, 70° C.	800 ,, ,, ,,	3

Pasteurised Grade A Tuberculin Tested Milk.

		Per 1000
Unheated fraction ..	20,000 bacteria per c.c.	1,000
Heated at 50° C.	15,500 ,, ,, ,,	775
,, ,, 55° C.	17,680 ,, ,, ,,	884
,, ,, 60° C.	14,060 ,, ,, ,,	753
,, ,, 65° C.	10,360 ,, ,, ,,	518
,, ,, 70° C.	1,260 ,, ,, ,,	68

These two tests are compared in Fig. 3.

Although the object of this communication is to draw attention to the principle of the test rather than to provide a detailed description of its application, it may not be out of place to add one or two practical details which have been found useful. It is difficult to make an even suspension of cheese in water, but a good suspension can be made by rubbing up small weighed fragments of cheese in egg

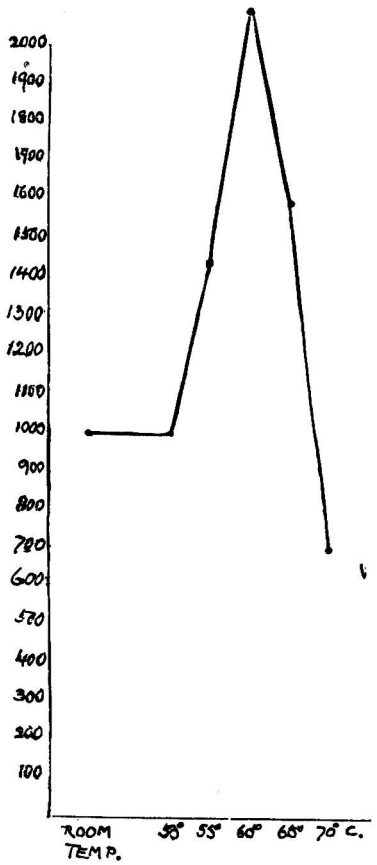


Fig. 2.

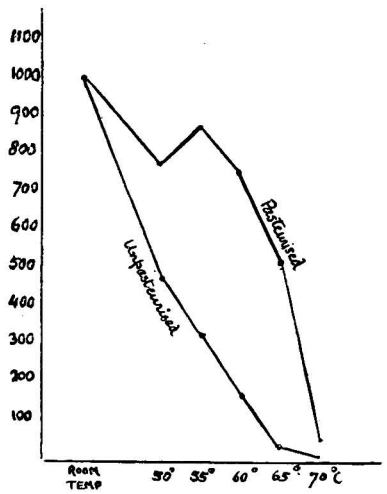


Fig. 3.

yolk. Convenient quantities to use for cheese are 1 grm. of cheese suspended in one egg yolk and diluted with sterile water to 1 per cent. Of this suspension, 1 c.c., 0·1 c.c. and 0·01 c.c. are plated. If very few bacteria are present, it may be necessary to work with a 10 per cent. suspension, but this makes the counting of the colonies more difficult.

In carrying out tests on milk it is usually more convenient to plate out 0·1, 0·01 and 0·001 c.c. The colonies visible to the naked eye are counted against a black back-ground. A magnifying glass is useful in helping to decide what to accept as a colony, but only the colonies visible to the unaided eye should be recorded.

The main difficulty in such work as this is the making of accurate dilutions, and, to avoid errors due to this cause, experiments are now being made with the use of large Petri dishes, 9 in. in diameter. No dilutions are made, but 1 c.c. from each fraction is mixed with 250 c.c. of agar and a big plate poured. Similar modifications may be necessary in applying the test to different types of food.

Discussion.

The President remarked that this was an interesting communication, and that the Society was indebted to Dr. Dukes for coming to present it to the members. He would like to ask, with regard to pasteurised milk, what was the interval between pasteurisation and the heating for the test. He wondered whether, if pasteurised milk were left for long, the bacteria surviving would re-establish themselves.

Mr. A. T. R. Mattick said that he was most interested in this paper, and congratulated Dr. Dukes. There was no doubt that, within obvious limitations, this test would be of value. The objection he saw (which Dr. Dukes himself appreciated) was the question of recontamination, particularly with milk. With pasteurised cheese, recontamination was not, perhaps, a serious factor, because this was wrapped in tin-foil and certain substances were added which might help to keep down bacteria; with milk it was a very serious factor. It was a fact that some pasteurising plants involved a waste of energy. Milk was heated for half-an-hour to 140° F., and then re-contaminated during subsequent handling, on the cooler and often in bottles. These bacteria had not had to survive a period of heating, and would therefore tend to give a different type of curve from those bacteria surviving one heating. So long a time elapsed before milk went to the analyst that multiplication of bacteria would have taken place, particularly with unpasteurised milk. He referred to thermophilic and thermoduric bacteria. Thermoduric quite easily withstood a temperature of 65 to 70° C., and would grow at ordinary temperatures, and those thermoduric in one generation would not necessarily be thermoduric in another. For cheese, so long as there was no contamination, Dr. Duke's findings might be perfectly sound. He referred to the fact that the thermal death-point of organisms in cheese was sometimes changed for some reason between first and second heating, and a thermal death-point at P_H 5·5 would be altered at P_H 6·5.

Mr. D. Clayson congratulated Dr. Dukes on his courage in compiling a paper dealing with bacteria in quantitative terms. Dr. Dukes, he remarked, had not dealt with the question of bacterial spores. It was quite possible for spores to be present in a pasteurised product and to prolificate and germinate. He mentioned the lactic acid streptococcus (not, however, a spore former) he had come across some milk he knew to have been pasteurised at 145° F. for half-an-hour, which had an abnormal number of streptococci, and he identified these as *Streptococcus thermophilus*. After re-pasteurising, he got some strains resembling the original and some differing from the original in that they curdled milk very slowly. He had traced out the difference between the resistance of these various strains. The strains collected in the normal way were killed completely at 145° F.—the other strains were rather more heat-resistant. He thought these organisms might upset the results rather seriously, and to make sure that he had not got a freak, he repeated the test with *Streptococcus acidi lactici* and got similar results.

Dr. H. E. Cox thought that the Society was fortunate in having this test brought before them, because it enabled one to tell whether other substances besides milk had been pasteurised. A chemical test was available for milk, but

he had vainly tried to find one applicable to cheese. He confirmed what Dr. Dukes had said about the method as applied to cheese, as he had had the opportunity of trying it. He asked what was the approximate number of organisms found by Dr. Dukes in pasteurised cheese. At least one large producer of cheese made it from pasteurised milk; was it possible to differentiate by Dr. Dukes' method whether cheese had been made from pasteurised milk or not? What was the best acidity of the plating medium used for the counts?

Mr. H. JEPHCOTT queried what was meant by the various speakers when they mentioned "pasteurised cheese." Did they mean "Processed Cheese" or cheese made from pasteurised milk, as there was a great difference?

Dr. DUKES, replying, said that when he was speaking of "Pasteurised Cheese" he had meant cheese which had been pasteurised after it had been converted into cheese. A great deal of the cheese sold now had been pasteurised, and it was to this type of cheese he referred. The interval after pasteurisation was a very important problem, but he had not been able to solve it, except that the test was certainly more trustworthy the sooner one carried it out after pasteurisation, and the most satisfactory curves were those from milk pasteurised at 2 p.m. with the test carried out at about 4 p.m. He would be inclined to say that the test would lose in value with the passage of time. Recontamination was the weak point in the practical value of the test, but, of course, it had to be borne in mind that recontamination was not carried out wilfully. Mr. Mattick had dealt with thermophilic and thermoduric bacteria. They certainly were a source of peculiar behaviour after re-heating.

The number of bacteria present in cheese was very variable. Ordinary fresh Cheddar cheese might contain 10,000,000, 20,000,000, or even 100,000,000 bacteria per grm., and then, on keeping, the numbers declined. In pasteurised cheese the numbers increased, so that, after a certain time, one got approximation.

With regard to the question whether the test was sufficiently delicate to show the difference in two raw cheeses, one made from fresh and the other from pasteurised milk: he could only say that he had tried it, and got a difference in the curves, but the difference was slight.

Standard media were used, the advantage being that by always using the same type of media, one grew the same kind of bacteria every time, and the results were comparable. He thanked the Society for allowing him to come there—he had thought the principle of the paper might interest the members. It had been a great honour and a great pleasure to speak.

The Changes with Age of the Hydrogen Ion Concentration of Egg White and Egg Yolk and of the Refractive Index of the Egg White.

By J. C. BAIRD, B.Sc., A.I.C., and J. H. PRENTICE, B.Sc., A.I.C.

(*Read at the Meeting, December* 4, 1929.)

Under the present regulations in Northern Ireland eggs are deemed to be stale if the air-space measures more than one-quarter of an inch in depth.

The investigations described here were made to determine the practicability of using the hydrogen ion concentration of egg yolk or egg white, or the refractive index of the egg white, as a means of determining the age of the egg in cases of legal dispute.

Healy and Peter* (*Amer. J. Physiol.*, 1925, **74**, 363), using colorimetric methods, found that there was a marked change in the reaction of the white, which rose from an initial figure of P_H 8·2 to P_H 9·5 at the end of eight days, and to 9·7 after twenty-eight days, whilst the P_H of the yolk showed little alteration until after three weeks, when the acidity began to decrease. As at this stage of their experiment only a single determination was made, it was felt that further work over an extended period and with a larger number of eggs might prove of value.

Gueylord and Portier* (*Nature*, 1925, **116**, 155), working with eggs which were undergoing incubation, found that in the early stages of incubation egg white is alkaline (P_H=8) and the egg yolk is acid (P_H=5·5), and they traced, during development, the convergence of these figures towards neutrality, which was reached on the tenth day.

Details of Experiments.—The determinations of hydrogen ion concentration were made by means of the quinhydrone electrode designed by Biilman (*J. Agric. Sci.*, 1924, **14**, 232) for determining P_H in soils. The apparatus proved very satisfactory in operation. The accuracy of results was confirmed by colorimetric tests. An Abbé refractometer was used to determine the refractive indices of the egg whites.

* The experimental work was in progress before it was possible to obtain copies of the original papers of Healy and Peter and of Gueylord and Portier.

The procedure adopted was as follows:—The egg was broken, and the white carefully separated from the yolk. Ten c.c. of white were immediately shaken up with 20 c.c. of water, together with a few mgrms. of quinhydrone, and the determination made. The yolk was repeatedly washed with distilled water and dried by rolling on filter paper. The membrane was then broken, and 10 c.c. of the contents used, as in the case of the white. It was found necessary to clean and ignite the platinum electrode after each determination.

All the eggs used (128) were laid on the same day by unmated pullets. The eggs were stored in the laboratory at room temperature (18° C.), and determinations made twice weekly, in the first series of investigations. In the light of these results a second series of experiments was carried out in which the readings were taken daily or twice daily.

The refractive index of the white was found to be very constant, and was not investigated in the second series. The values obtained lay between 1·369 and 1·356.

The results for the ionic concentrations obtained for the first series are given in Table I and plotted in the Graph, those from the second series in Table II. The results of each determination are given in Table II, from which it may be seen that the agreement between individual readings in each age-group was satisfactory.

TABLE I.

Age of eggs in days.	No. of eggs.	Average P_H. White.	Yolk.
1	6	8·36	6·04
2	12	8·54	6·01
5	4	8·93	5·97
8	5	9·01	6·05
12	5	9·01	6·03
15	5	9·03	6·05
19	4	9·08	6·02
22	4	8·98	6·09
26	6	8·93	6·03
29	4	9·02	6·01
33	6	9·00	6·22
36	5	9·03	6·07
39	3	9·03	6·16
43	6	9·06	6·18
46	5	9·07	6·18
53	5	8·97	6·33
57	6	9·06	6·22
60	3	9·16	6·17
64	3	9·06	6·24
67	3	9·01	6·28
71	3	8·98	6·31

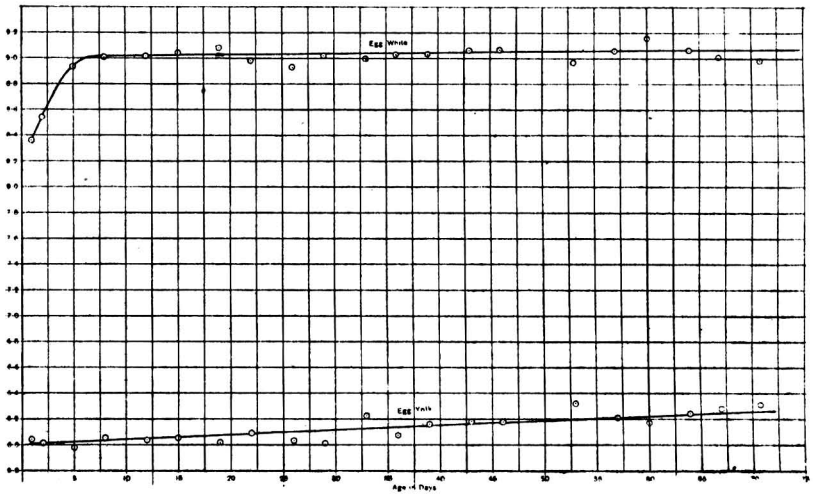


TABLE II.

Age in hours.	No. of eggs.	P_H of white.	P_H of white. Average.	P_H of yolk.	P_H of yolk. Average.
2	4	7·65	7·63	6·08	6·05
		7·61		6·08	
		7·62		—	
		7·63		6·00	
8	3	8·17	8·21	6·10	6·07
		8·15		6·07	
		8·31		6·05	
18	3	8·37	8·34	6·05	6·04
		8·34		5·99	
		8·31		6·08	
44	3	8·46	8·51	6·04	6·04
		8·54		6·03	
		8·53		6·05	
68	3	8·79	8·76	6·08	6·05
		8·77		6·02	
		8·72		6·05	
98	3	8·81	8·83	6·07	6·01
		8·76		5·96	
		8·91		6·00	
164	2	8·95	8·99	6·02	5·99
		9·03		5·96	

The results obtained indicate that the normal P_H of fresh egg white is approximately 7·6, and that there is a rapid rise in the course of the first week of storage to a level of about P_H 9·0, at which figure the P_H remains fairly constant.

The fresh yolk gives a reaction of approximately P_H 6·0, which, in the course of ten weeks, rises to about 6·2.

These findings confirm the work of Healy and Peter, already cited. As a criterion of the freshness of commercial consignments of eggs, the P_H of either yolk or white appears to be of no practical importance, since commercial eggs are generally at least several days old, and it is after this period that any means of determining age becomes of most value. Further, the recent work of Sharp (*Science*, 1929, **69**, 278) shows that the storage of eggs in an atmosphere containing small percentages of added carbon dioxide arrests the change in P_H of the white, and it remains constant at the initial figure of 7·6. Such conditions would, of course, prevent the hydrogen ion concentration being used as a measure of age.

SUMMARY.—The P_H of the white of freshly laid eggs was found to be 7·63, and the P_H of the yolk 6·0.

The P_H of the white changed rapidly during the first seven days and reached a constant figure of approximately 9·0.

The reaction of the yolk was not quite constant, but rose very gradually.

As a means of determining the age of commercial eggs the hydrogen ion concentration of yolk or white is of no value.

The refractive index of the white is constant at a figure of 1·360.

AGRICULTURAL CHEMISTRY DEPARTMENT,
QUEENS' UNIVERSITY, BELFAST.

A Study of the Methods of Determining Boron Compounds in Food and Drugs.

BY A. SCOTT DODD, B.Sc., PH.D., F.I.C.

(Work done under the Analytical Investigation Scheme.)

PART III. EXPERIMENTAL: THE CONDITIONS REQUIRED FOR QUANTITATIVE TITRATION.

THE interaction of boric acid with numerous organic compounds has also been studied by Magnanini (*Z. physikal. Chem.*, 1890, **6**, 58; 1892, **9**, 230; 1893, **11**, 281), who found that in aqueous or alcoholic solution boric acid interacts with all hydroxy-carboxylic acids in which at least one hydroxyl group is in the α-position to a carboxylic group, the complex acids formed being stronger than the organic acid from which they were produced. The other organic acids do not interact with boric acid in solution.

THE USE OF HYDROLYSED MILK SUGAR AND GALACTOSE TO AID THE TITRATION OF BORIC ACID SOLUTION.—Gilmour (*loc. cit.*) studied the behaviour of various carbohydrates when used to aid the titration of boric acid solutions, and found that lactose could not be employed successfully.

The following experiment was made by me to ascertain whether boric acid could be titrated in presence of hydrolysed milk sugar;

Twenty grms. of milk sugar were dissolved in 20 c.c. of water, and the solution boiled. Two c.c. of 0·5 *N* hydrochloric acid were added, and the test tube and contents were heated in boiling water for 5 minutes and shaken well. The solution was then cooled, diluted, neutralised with 2 c.c. 0·5 *N* sodium hydroxide solution, and made up to 100 c.c. Five c.c. of invert milk sugar solution (= 1 grm. of milk sugar) were added in one operation to 5 c.c. of approximately 0·1 *N* boric acid solution, and this was titrated with 0·1 *N* sodium hydroxide solution, phenolphthalein being used as indicator. The end-point was noted when the solution became permanently pink.

TABLE X.

Boric acid solution. c.c.	Milk sugar hydrolysed. Grms.	Total liquid. c.c.	0·1 *N* NaOH. c.c.
5	1	12·2	2·2
5	2	18·2	3·2
5	3	23·5	3·5
5	4	28·7	3·7
5	5	34·1	4·1
5	6	39·4	4·4
5	7	44·5	4·5
Evaporated to dryness and 5 c.c. water added :			
5	7	10·25	5·25
0·5 *grm. mannitol added :*			
5	7	10·25	5·25

(5 c.c. of boric acid solution + 0·5 grm. of mannitol when titrated required 5·25 c.c. 0·1 *N* NaOH = 0·0325 grm. H_3BO_3.)

The above experiment shows that it is possible to obtain a correct titration of boric acid by using inverted milk sugar, but that the presence of much water tends to militate against the end-point being arrived at speedily. This was corroborated as follows:—Twenty-five c.c. (=5·0 grms. of milk sugar) of the hydrolysed milk sugar solution were evaporated to dryness. Five c.c. of 0·1 *N* boric acid solution were added. The contents of the basin were heated until dissolved, and then cooled and titrated.

The boric acid on titration required 5·25 c.c. of 0·1 *N* sodium hydroxide solution.

The end-point was quite sharp, and the titration was very similar in behaviour to that when using 0·5 grm. of mannitol. The total liquid present was between 10 and 11 c.c. This experiment shows that 5 grms. of milk sugar, inverted and dried, are capable of ensuring the accurate titration of 5 c.c. of boric acid solution or 0·0325 grm. of boric acid.

Ten grms. of galactose were dissolved in 10 c.c. of distilled water, with heating. The solution was diluted, cooled, and made up to 50 c.c.

Ten c.c. of boric acid solution consumed 10·5 c.c. of 0·1 *N* sodium hydroxide solution, 0·5 grm. of mannitol and phenolphthalein being used (*i.e.* 10 c.c. of boric acid solution = 0·065 grm. of H_3BO_3).

Ten c.c. of boric acid solution (= 0·065 grm. H_3BO_3) were placed in a titrating basin and titrated with 0·1 *N* NaOH solution, with phenolphthalein as indicator, successive additions of the galactose solution in quantities of 5 c.c. at a time (*i.e.* 1 grm. of galactose) being made. The results were as tabulated below:

TABLE XI.

Boric acid solution. c.c.	Galactose. Grms.	Total liquid. c.c.	0·1 *N* NaOH. c.c.
10	1	22·0	7·0
10	2	28·0	8·0
10	3	33·8	8·8
10	4	39·2	9·2
10	5	44·7	9·7
10	6	49·9	9·9
10	7	55·1	10·1
10	8	60·2	10·2
10	10	60·2	10·5
10	0·5 grm. mannitol added	60·2	10·5

This experiment shows that galactose may be used satisfactorily in the titrating of boric acid solutions, but that a solution of galactose is not satisfactory, in view of the diluting effect of each addition. The advantage of using solid galactose is demonstrated by the following results, which were obtained when successive quantities of solid galactose were added:

TABLE XII.

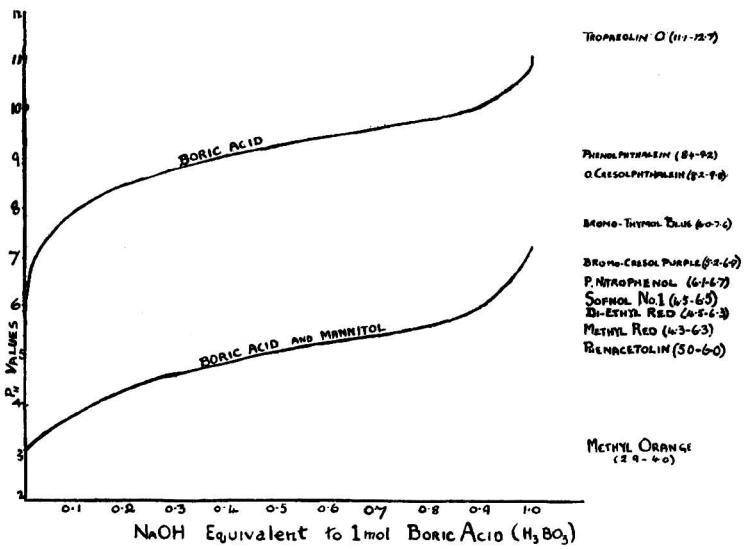
Boric acid solution. c.c.	Galactose. Grms.	Total liquid. c.c.	0·1 *N* NaOH. c.c.
10	5	20·3	10·3
10	6	20·4	10·4
10	7	20·5	10·5
10	8	20·5	10·5

The end-point was quite sharp. In both series of experiments in which hydrolysed milk sugar and galactose were used the reaction was not so distinct as when mannitol was employed, but it was distinct enough to enable one to rely on the result. It is interesting to note that, whereas when glycerol is used it has to be present to the extent of one-third of the total solution, in the present experiment, in which galactose was used, 7 grms. of that sugar had to be added to about three times that number of c.c. of liquid. This may, however, be merely a coincidence, but the above series of experiments has clearly demonstrated that boric acid solutions can be accurately titrated with the aid of hydrolysed milk sugar or galactose. As the former consists of a mixture of dextrose and galactose and, according to Gilmour, the dextrose is of little or no assistance in stabilising the meta-boric acid, one must conclude that galactose acts similarly to fructose in forming a comparatively stable complex with boric acid. Gilmour claimed certain

economic advantages in the discovery of invert sugar as an aid to titrating boric acid solutions, but no such advantages can be claimed for hydrolysed milk sugar or galactose. The knowledge that these substances can be used successfully, may, however, be regarded as being of some theoretical interest.

It is interesting to note that the complex acids formed by the interaction of hydrolysed milk sugar or galactose with boric acid are much stronger than boric acid itself, and that the extent to which these complex acids are formed in solution increases with concentration and diminishes with dilution.

EXPERIMENTS RELATIVE TO THE CHOICE OF SUITABLE INDICATORS FOR THE DETERMINATION OF BORIC ACID.—Boric acid behaves as a very weak mono-basic acid, $HBO_2.H_2O$, and, as shown in the figure, has a titration curve varying from about P_H 6 to about P_H 11. It is, therefore, impossible to titrate a solution of



boric acid direct, except with an indicator which changes colour at a P_H greater than 11, and, for this reason, tropaeolin O (11·1 to 12·7) has been suggested by E. B. R. Prideaux (*Z. anorg. Chem.*, 1913, **83**, 362). In order to eliminate any acidity due to the presence of other acids, preliminary neutralisation of these is required. This can only be done colorimetrically, with the aid of an indicator which gives a colour change below P_H 6, or so little above P_H 6 as to cause only a negligible error. Methyl orange was, therefore, chosen as a suitable preliminary indicator, as its P_H range (2·9 to 4·0) is so far below 6 that it is unaffected by boric acid solutions. Methyl orange, however, is far from being ideal for this purpose, as the end-point is not very sharp unless concentrated solutions are being employed, and a theoretical error is introduced by its P_H value being so far from P_{H6}. The ideal preliminary indicator is one which is nearly colourless in the presence of alkalis, and has a sharp reaction, which coincides with the P_H value of the boric acid solution under examination.

The addition of an excessive amount of mannitol increases the acidic intensity of a solution of boric acid from P_H 6 to about P_H 3, and the end-point of the acid complex formed by boric acid and mannitol is in close proximity to P_H 7·2. The final titration of solutions of boric acid and excess of mannitol can, therefore, be made with the aid of any indicator which reacts sharply with alkalis at a P_H higher than 7·2. The ideal indicator is one which reacts sharply at P_H value close to, but slightly higher than, the P_H of the end-point of the titration of the mannitol and boric acid complex with sodium hydroxide solution. Phenolphthalein has a sharp colour change, but its P_H range (8·4 to 9·2) is distinctly higher than the neutral point of the titration. Bearing these theoretical considerations in view, the experiments shown in the following table were carried out:

EXPERIMENTS WITH VARIOUS INDICATORS.—Ten c.c. of approximately 0·1 *N* boric acid + 60 c.c. of water were placed in a porcelain basin and acidified with 5 drops of *N* sulphuric acid, boiled for 5 minutes, and cooled quickly. The liquid was neutralised with 0·05 *N* sodium hydroxide solution, different indicators being used. The final titration, after adding excess of mannitol, was carried out with the aid of different indicators.

TABLE XIII.

1st Indicator.	End-point.	Final Indicator.	End-Point.	Final titration. 0·05 *N* NaOH. c.c.	Final titration. $=H_3BO_3$ Grm.
(1) Methyl orange (2·9–4) ..	Indefinite	Phenolphthalein (8·4–9·2)	Sharp	20·25	0·0628
(2) Methyl red (4·2–6·3)	Sharp	,,	,,	20·30	0·0629
(3) Di-ethyl red (4·5–6·3)	,,	,,	,,	20·32	0·0630
(4) Sofnol No. 1 (4·5–6·5)	,,	,,	,,	20·32	0·0630
(5) *p*-Nitrophenol (6·1–6·7) ..	,,	,,	,,	20·32	0·0630
(6) Brom-cresol purple (5·2–6·8) ..	,,	,,	,,	20·33	0·0630
(7) Phenacetolin (5·0–6·0) ..	,,	,,	,,	20·32	0·0630
(8) Brom-thymol blue (6·0–7·60) ..	,,	,,	,,	20·32	0·0630
(9) Methyl red	,,	Brom-thymol blue	Indef. green	19·90	0·0617
(10) Di-ethyl red	,,	(6·0–7·6)	and blue	20·20	0·0626
(11) Sofnol No. 1	,,	,,	,,	20·25	0·0628
(12) *p*-Nitrophenol	,,	,,	,,	20·20	0·0626
(13) Brom-cresol purple	,,	,,	,,	20·25	0·0628
(14) Phenacetolin	,,	,,	,,	20·27	0·0628
(15) Brom-thymol blue	,,	,,	,,	20·20	0·0626
(16) —	—	Phenolphthalein	Sharp	20·32	0·0630

As is shown in Table XIII, accurate results can be obtained with 0·063 grm. of boric acid (H_3BO_3), by the use of methyl red, di-ethyl red, Sofnol No. 1, *p*-nitrophenol, brom-cresol purple, phenacetolin or brom-thymol blue as preliminary indicators, and phenolphthalein as the final indicator. The reaction of the preliminary indicators was sharp in each case, but the sharpness of the final

titration was obscured by the presence of certain indicators with the phenolphthalein. *p*-Nitrophenol gave a dirty green colour, brom-cresol purple and brom-thymol blue gave a blue colour, and phenacetolin a pink colour some time before the end of the titration was reached, but when a sufficient quantity of phenolphthalein was present, the end-point was, nevertheless, quite readily observed. Brom-thymol blue proved to be quite unsuitable for a final indicator, as the end-point was rendered indefinite by the blue colour reaching its maximum very gradually.

Cresolphthalein (P_H 8·2 to 9·8) and thymol blue were also tried as final indicators, but showed no advantage over phenolphthalein. Owing to its sharpness of reaction, there is little doubt that phenolphthalein is as satisfactory an indicator as one could desire.

EXPERIMENTS RELATIVE TO THE DETERMINATION OF BORIC ACID IN SOLUTIONS OF VARIOUS CONCENTRATIONS.—The difficulty of observing the point of neutrality, when neutralising concentrated solutions of boric acid or borates, led to an attempt being made to ascertain whether the accuracy of the determination would be impaired by working on smaller quantities at greater dilution.

The Pharmacopoeias of Great Britain, Germany and U.S.A. give methods for testing the purity of borax. The first two use 2 grms., and the last 5 grms. of the sample, employ methyl orange as a neutralising indicator, and normal sodium hydroxide solution, glycerol and phenolphthalein for the determination of the boric acid. In carrying out this test it was obvious that the accuracy of the final titration suffered through lack of sharpness of reaction of the methyl orange, due partly to the unsatisfactory nature of this indicator and partly to the buffer action of the borate solution. The following experiments were tried:—Five grms. of pure boric acid were dissolved in water and made up to 100 c.c. Four portions of 20 c.c. each were placed in four porcelain titrating basins, and in three of them, 20 c.c. of water and 2 drops of *N* sulphuric acid were placed. Twenty c.c. of water were also added to the contents of the fourth basin, together with excess of mannitol and a few drops of phenolphthalein solution. On titrating with *N* sodium hydroxide solution this portion consumed 16·28 c.c. (The remaining 20 c.c. of boric acid solution in the flask were mixed with 20 c.c. of water and tested with a drop of brom-cresol purple. A faint blue tinge of colour was produced, which showed that this solution was practically neutral.) The contents of the other three basins were tested as follows:

(1) Sofnol No. 1 as preliminary indicator (neutral-point rather indefinite). Final titration = 16·10 c.c. *N* NaOH.

(2) Brom-cresol purple as preliminary indicator (neutral-point somewhat indefinite but slightly better than with Sofnol No. 1). Final titration = 16·30 c.c. *N* NaOH.

(3) Methyl orange as preliminary indicator (neutral-point very indefinite). Final titration = 16·15 c.c. *N* NaOH.

It was found by additional tests that, with solutions containing 1 grm. or more of boric acid, it was practically impossible to be certain of the exact neutral point with methyl orange to within 0·1 c.c. of *N* sodium hydroxide solution.

With brom-cresol purple, methyl red, di-ethyl red, and Sofnol No. 1, a solution containing 0·1 grm. of boric acid (H_3BO_3), diluted to 40 c.c., gave an accurate indication of neutrality to within 0·02 c.c. of 0·1 *N* sodium hydroxide solution.

A solution containing 0·1 grm. of boric acid in 40 c.c. (=0·25 per cent.) had an acidity similar to 0·10 c.c. of 0·01 *N* hydrochloric acid in 40 c.c. of water. The addition of 0·08 c.c. of 0·01 *N* hydrochloric acid to the boric acid solution gave a distinct reaction with Sofnol Indicator No. 1.

In using methyl orange it has been found that the error may amount to 0·1 c.c. of *N* sodium hydroxide solution, when the determination is being made on 1 grm. of boric acid. That is, the error due to faulty neutralising may amount to 0·0062 grm. in 1 grm., or 0·62 per cent.

When using a solution containing 0·1 grm. of boric acid in 40 c.c. of water and any of the following indicators: Sofnol No. 1, methyl red, di-ethyl red, or brom-cresol purple, the maximum error was found to be about 0·02 c.c. of 0·1 *N* sodium hydroxide solution. Therefore, the actual maximum error in 0·1 grm. of boric acid is equivalent to 0·00124 grm. of boric acid or 0·124 per cent.

These results show clearly that greater accuracy can be obtained by determining boric acid in dilute solutions than in concentrated solutions. There are, in fact, several disadvantages in using concentrated solutions, and nothing is to be gained by their use. In analysing samples containing a high percentage of boron it is advisable to make a solution therefrom, and to make the determination on an aliquot part containing about 0·1 grm. or less of boric acid by means of 0·1 *N* or 0·05 *N* sodium hydroxide solution.

MODIFICATION OF THE B.P. METHOD OF TITRATING BORIC ACID AND BORAX.—It was found by experiment that accurate results and more satisfactory working were obtained by using for each estimation one-tenth of the quantity of boric acid or borax stated in the B.P., and titrating with 0·1 *N* solutions instead of *N* solutions. Care must be taken, however, to use distilled water free from carbon dioxide, and methyl red, or Sofnol No. 1, and mannitol may, with advantage, be used in place of methyl orange and glycerol, respectively. The quantity for each analysis consists of 10 c.c. of a solution of 1 grm. of boric acid or 2 grms. of borax in 100 c.c. of distilled water, and should be diluted with 20 c.c. of water before titrating.

The use of mannitol in place of glycerol, as mentioned in the pharmacopoeias, is a great improvement, as it is much more easily handled, gives a sharper reaction, and is more likely to be neutral. Another advantage of using small quantities of boric acid and borates for each determination is that much less mannitol is required.

The foregoing experimental details show that sufficiently accurate results may be obtained by the use of several different indicators. The choice is, in fact,

in many instances, merely a matter of personal preference on the part of the chemist. As the result of experience and these experimental tests I have a distinct preference for Sofnol Indicator No. 1, as a preliminary indicator, and have found no indicator better than phenolphthalein for the final titration. These indicators leave nothing to be desired when determining boric acid in dilute solutions containing 0·25 per cent. of boric acid or less.

MODIFICATION OF R. T. THOMSON'S METHOD.—A method such as that described in the ANALYST (1923, **48**, 416) is so comprehensive as to be of general application for all samples. There are, however, some points where the analyst can with advantage introduce modifications and curtailments, which the nature of the sample under examination may suggest. Omitting substances such as butter, margarine and egg melanges, in which boric acid is probably most readily determined by special methods, one can conveniently divide the other substances into two classes, namely, (1) samples containing 8 per cent. of oil and over, and (2) samples containing less than 8 per cent. of oil. The treatment is as follows:

Samples containing 8 *per cent. of oil and over.*—Weigh out 20 grms. of the sample, in a state of fairly fine division, in a platinum (or gold-platinum alloy) basin, render it distinctly alkaline with *N* sodium hydroxide solution, as indicated by adding a few drops of phenolphthalein solution, and dry in a steam-oven. Stir the dry residue with successive portions of petroleum spirit and filter into a separator. Wash the filter paper and contents with petroleum spirit until free from fat and place them in the basin. Wash the petroleum spirit extract in a separator with 5 c.c. of *N* sodium hydroxide solution, and then with 5 to 6 c.c. of water, and run all the washings into the platinum basin. Add another 5 c.c. of *N* sodium hydroxide solution to the contents of the basin and stir. Evaporate on a steam-oven, then heat, and thoroughly char over an Argand burner. The charred mass is now in a condition for extracting.

Samples containing less than 8 *per cent. of oil.*—Weigh out 20 grms. of the sample in a state of fairly fine division, in a platinum (or gold-platinum alloy) basin, render alkaline with *N* sodium hydroxide solution as indicated by adding a few drops of phenolphthalein solution. Then add 5 c.c. of *N* sodium hydroxide solution in excess, evaporate on a steam-bath, heat and thoroughly char over an Argand burner.

Treatment of the charred mass.—Transfer the charred mass to a porcelain mortar, grind up and return to the platinum basin, rinsing out the mortar with about 10 to 15 c.c. of water. Heat the contents of the basin, filter into a small beaker, and wash with about 5 c.c. of water (boiling). Place the filter paper and charred contents in the platinum basin, evaporate and ignite to a white ash at a dull red heat.

Transfer the contents of the small beaker to the platinum basin, cover this with a glass plate and run in dilute hydrochloric acid from a pipette until the contents are distinctly acid. Place the platinum basin on the steam-bath, and, after the effervescence due to the escape of carbonic anhydride has ceased, wash the glass plate into the basin and continue the heating until the contents have evaporated

to about half bulk. Filter into a 100 c.c. flask, wash the filter paper thoroughly with small quantities of boiling water, and, for convenience of working, leave the flask not more than three parts full. To the contents of the flask add 3 c.c. of 10 per cent. calcium chloride solution and 5 drops of phenolphthalein solution. Then add *N* sodium hydroxide solution, with constant shaking, drop by drop, until the contents are faintly pink. Make up to the 100 c.c. mark with water, shake thoroughly and filter.

Measure 50 c.c. of the filtrate into a white porcelain titrating basin, add 5 or 6 drops of *N* sulphuric acid in excess of that required to discharge the pink colour of the phenolphthalein, boil for 5 minutes, with constant stirring, to expel the carbon dioxide, and cool quickly by placing the basin in cold water. Add to the contents, which should be distinctly acid, 1 drop of a solution of Sofnol Indicator No. 1, and carefully neutralise with 0·1 *N* sodium hydroxide solution. Add about 0·5 grm. of mannitol, together with 10 drops of phenolphthalein solution, and titrate with 0·1 *N* sodium hydroxide solution until a distinct pink colour is indicated by the phenolphthalein. If, on the addition of another portion of mannitol, the colour is not discharged, the titration is now considered complete.

In order to ascertain if the phosphates have been completely precipitated, pour the contents of the titrating basin into a beaker flask, acidify with acetic acid, add a few drops of ammonium oxalate solution and warm. A positive reaction indicates that sufficient calcium chloride has been added to precipitate all the phosphates.

The number of c.c. of 0·1 *N* sodium hydroxide solution consumed in the titration, multiplied by 0·062, gives the percentage of boric acid (H_3BO_3).

Special precautions.—(1) As shown by the foregoing experiments (ANALYST, 1929, **54**, 715), boric acid and borates are soluble in methylated ether, even when reasonable precaution is taken to ensure the dryness of both the solvent and the boron compounds. It is, therefore, better to use petroleum spirit to extract the oil, when this operation is necessary, as this solvent does not extract nearly so much of the boron compounds, and the risk of loss in the process of re-extraction is thereby reduced to a minimum.

(2) The complete extraction of all the boron compounds from the ash of samples is by no means easy, especially when much mineral matter is present, unless the ignition is complete and all the carbonaceous matter removed. For this reason, double and sometimes more frequent ashing and extraction is necessary. Sufficient hydrochloric acid must be added to decompose completely the borates formed.

(3) The danger of loss of borates by precipitation along with the phosphates has already been mentioned in THE ANALYST (1923, **48**, 416). Care must, therefore, be taken to avoid adding any excess of alkali more than that necessary just to precipitate the phosphates and no calcium borate. The exact point is that at which the clear supernatant liquid shows the first tinge of pink. When the precipitate is moderately large it is necessary, therefore, to allow the precipitate to settle before the reaction can be correctly observed.

(4) Before proceeding to the final titration it is necessary to eliminate the last traces of carbon dioxide. This, however, must be done with caution, as boric acid is to a certain extent volatile in acid solutions. The foregoing experiments dealing with this point show that, if reasonable care is taken, no loss of boric acid will occur. For convenience of working, a titrating basin is preferable to a glass beaker. The elimination of carbon dioxide is much more rapid and complete, but it is absolutely necessary to give the operation undivided attention during the 5 minutes of boiling, to prevent loss of boric acid by spurting or over-heating at the edges of the liquid.

(5) When dealing with substances containing only minute quantities of boron compounds the indication of the neutral point prior to the final titration must be sharp and carefully reached by final adjustment with fractions of a drop of 0·1 *N* sodium hydroxide solution. The sharpness of this reaction when using Sofnol Indicator No. 1 presents no difficulty if the phosphates and carbon dioxide have been completely eliminated.

SUMMARY.—The following points were ascertained by these investigations:

Experiments relative to the separation from organic matter.—(1) That oil or fat cannot be completely separated from boron compounds in articles of food by extraction with methylated ether, petroleum spirit, benzene, chloroform or carbon tetrachloride. Benzene and petroleum spirit were found to extract practically no boric acid or sodium borate, when the solvents and the samples were perfectly dry, but, as the presence of minute traces of moisture or alcohol increased the solubility of the boron compounds, it was found to be advisable either to re-extract these with a solution of caustic alkali or to titrate the boric acid direct if phosphates were absent. Benzene and petroleum spirit were, therefore, considered to be more suitable than methylated ether for extracting oil and fat.

(2) That boron compounds when ignited with excess of caustic alkali, either alone or along with substances which do not contain glycerol or glycerides, do not volatilise appreciably. When, however, boron compounds are ignited with excess of caustic alkali together with substances which contain glycerol or glycerides, considerable loss of boron results.

(3) The loss depends upon the degree of contact between the boron compounds and the glyceride, and the amount of the latter present.

(4) The loss of boron compounds is proportional to the percentage of the glyceride present in the sample, and is fairly constant for the particular kind of oil present, and apparently bears a definite relationship to the constitution of the oil and the percentage of glyceride therein.

(5) That, so long as the percentage of the glyceride is in excess, the quantity of the glyceride is immaterial, and causes the same percentage loss of boric acid on ignition with excess of alkali as another excessive quantity of that particular glyceride.

(6) That the loss of boron compounds, when ignited in presence of excess of alkali in an open basin, is slightly greater in highly inflammable substances than in those that burn more slowly.

(7) That, when less than 8 per cent. of fat or oil is present, direct ignition in presence of excess of alkali gives as accurate results as those obtained by previous extraction of the oil. In other words, it is unnecessary to separate the fat when its amount is less than 8 per cent.

(8) That the presence in the ash of a high percentage of salts, which form borates of low solubility, renders the complete extraction of the boron compounds very difficult and necessitates special treatment.

Experiments relative to the volatility of boric acid in acid solutions.—(9) That considerable loss of boric acid results from the evaporation of acidified solutions of boric acid. If, however, the boric acid solutions are very dilute, practically no loss takes place when such acidified solutions are boiled for 5 minutes with constant stirring, and evaporation does not exceed one-half of the original volume.

Experiments relative to the titration of boric acid solutions.—(10) That hydrolysed milk sugar or galactose may be used in place of glycerol or mannitol in the titration of boric acid, but that their use is unsuitable.

(11) That errors are likely to be caused in attempting to neutralise mixtures containing concentrated solutions of boric acid and strong acids, owing to the indefiniteness of the end-point, due to buffer action. The error when using methyl orange may amount to 0·62 per cent.

(12) That greater accuracy can be attained by making dilute solutions of borates or boric acid and carrying out the determination on small quantities (about 0·1 grm. or less), using either 0·05 *N* or 0·1 *N* sodium hydroxide solution, than by carrying out the estimation with 1 grm. or more of boric acid and using 0·5 *N* or *N* solutions of alkali.

(13) That, in determining boric acid in dilute solutions (0·1 grm. or less H_3BO_3 in 40 c.c.), the best indicators to use for preliminary neutralisation of extraneous acids are methyl red, di-ethyl red, Sofnol Indicator No. 1, and brom-cresol purple. These have a limit of accuracy well within 0·12 per cent. for a solution of the above strength and show considerably greater accuracy for more dilute solutions of boric acid.

(14) That mannitol is the most suitable substance for forming an acid complex with boric acid.

(15) That phenolphthalein and cresolphthalein are equally suitable for the final titration of boric acid solutions, and leave little to be desired from a practical point of view. They are much better than thymol blue or brom-thymol blue, as the end-point, when using either of these, is partly obscured by prolonged transition from green to blue.

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.

IRON KETTLES TINNED WITH TIN-LEAD ALLOYS.

THIS case, submitted to us in our general practice, appears to be of sufficient importance to justify us in publishing the details of it. Iron kettles, tinned inside, made by two manufacturers, were sent to us for examination.

Analysis of the tinning showed that the coating consisted not of tin, but of a tin-lead alloy, composed of 1 part of tin to 2 parts of lead.

Newcastle Town Water was boiled in a kettle of each make for twenty-four hours, the water being replaced from time to time, and the water replaced was reserved for analysis. Even in this short time the coatings were penetrated, and spots of rust appeared at the places where penetration occurred; the water contained both tin and lead.

Sections of known areas were cut from the sides of the kettles and were boiled in similar water for sixteen hours, the water being replaced from time to time, and that removed reserved for analysis. It was found that 1·5 mgrms. of lead were dissolved by the water from 100 sq. cm. of the tinned iron.

The hardness of the water of Newcastle-upon-Tyne varies between 7° and 14°, according to the proportion of moorland water contained in it; at the time these experiments were made the water had 7° hardness. As this water has no sensible solvent action upon lead, we attribute the effects to electrolytic action; the rapidity of the action would seem to confirm this.

It appears to us to be very dangerous to use tin-lead alloys for coating the insides of kettles, as lead poisoning might easily arise from it, and, the source of the poisoning being unsuspected, the illness would be ascribed to other causes.

PUBLIC ANALYST'S LABORATORY,
10, DEAN STREET, NEWCASTLE-ON-TYNE.

J. T. DUNN.
H. CHARLES L. BLOXAM.

A COLOUR REACTION BETWEEN NAPHTHOL YELLOW AND HYDROSULPHITES. A TEST FOR BOTH SUBSTANCES.*

A SCHEME for the separation and detection of Manchester yellow (2.4 dinitro-1-naphthol) in the presence of other prohibited dyes has been devised by J. R. Nicholls (ANALYST, 1927, **52**, 585; 1929, **54**, 335). To these tests the one to be described should make a useful addition.

When a centigramme or so of sodium hydrosulphite is added to a solution of either Manchester yellow or its sulphonic acid, naphthol yellow, a red colour is developed. In dilute, weakly alkaline solutions, the colour is a rose-pink. This colour is rather fugitive, acids in particular changing it to a yellow which soon fades, but the tint remains unchanged for several minutes if ammonia is present. In the presence of caustic alkalis or sulphites the coloration tends to an orange shade.

* Communication No. H421 from the Kodak Research Laboratories.

To apply the test, a couple of drops of strong ammonia are added to a few c.c. of the very dilute dye in a test tube, and a very small amount of solid hydrosulphite is added. The reactions of various dyes are given in the following table:—

No. in Colour Index, 1924.	Name.	Reaction.
9.	Manchester yellow	Rose colour
10.	Naphthol yellow	Rose colour
—	2.4.5-trinitro-1-naphthol	Pale salmon-pink
—	2.4.7-trinitro-1-naphthol	Pale salmon-pink
8.	Victoria yellow	Orange
7.	Picric acid	Brownish shade
801.	Quinoline yellow S.	No change
640.	Tartrazine	No change
1.	Dinitroso-resorcinol	Purple
2.	α-Nitroso-β-naphthol	Fades somewhat
3.	β-Nitroso-α-naphthol	Fades somewhat
365.	Chrysophenine	No change
655.	Auramine	No change
16.	Acid yellow	No change
20.	Chrysoidine	No change
766.	Fluorescein	No change
12.	Aurantia	Very pale brownish shade.

It has been found advisable to dilute the dye solution until it has the same depth of shade as a 0·02 per cent. solution of naphthol yellow which is used as a check. Under these conditions the orange colour given by Victoria yellow is stronger than the pink given by the dinitronaphthol dyes, and picric acid gives a strong brownish colour. In the absence of other dyes, this test will indicate the presence of 0·004 mgrm. of Manchester or naphthol yellow in 1 c.c. of water.

The test can be applied to mixtures of naphthol yellow with other yellow dyes which do not give the colour change. The change with such mixtures is to an orange colour.

In order to apply the test to the detection of hydrosulphites, a few mgrms. of the solid substance, or 1 c.c. of the solution, if the solid is not available, are added to a few c.c. of *N*-ammonia solution containing 0·02 per cent. of naphthol yellow. A rose colour indicates the presence of a hydrosulphite. The following reducing agents do not give the reaction:—Sodium formaldehyde sulphoxylate, sodium sulphide, sulphurous acid and its salts, thiosulphates, polythionates, salts of hydroxylamine or hydrazine, stannous salts, titanous salts, ferrous salts or sodium amalgam.

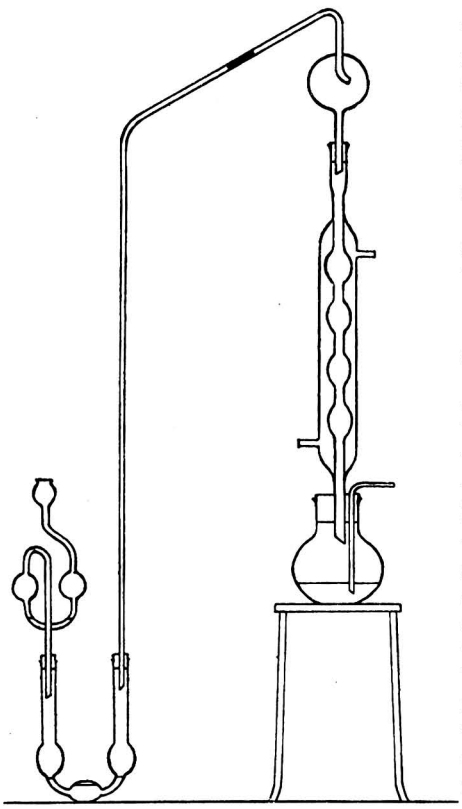
E. E. JELLEY.

RESEARCH LABORATORY,
KODAK LTD., WEALDSTONE.

A RAPID LIMIT TEST FOR THE DETECTION AND DETERMINATION OF SULPHUR DIOXIDE IN FOODS.

Two modifications of the Monier-Williams' process (ANALYST, 1927, **52**, 415) have been devised with the object of rendering that method more applicable to small quantities of material. The first consists in omitting the water used to dilute the sample, and thereby saving the time required to de-aerate the water in the flask. The second consists in using a much stronger acid solution, so as to effect more rapid liberation of the combined sulphur dioxide.

As accurate results could not be insured by distilling the sulphur dioxide into barium chloride and hydrogen peroxide solution and matching the turbidity with that produced by a standard, I have used a mixture of barium benzene sulphonate and hydrogen peroxide, and have subsequently titrated the free benzene sulphonic acid, instead of the free sulphuric acid as in the Monier-Williams' method.



Direct titration of the turbid solution, with bromphenol blue as indicator, was found difficult, owing to variations in degree of dilution and turbidity making the final end-point obscure, but by filtering the liquid into a Nessler glass and titrating with $N/50$ sodium hydroxide solution, very accurate results were obtained.

The apparatus required is shown in the accompanying diagram, and the details of the method are as follows:—

Thirty-five c.c. of hydrochloric acid (300 c.c. to 1800 c.c. of de-aerated water) are siphoned into the carbon dioxide flask (250 c.c. capacity); 3·5 c.c. of hydrogen peroxide (15 c.c. of Merck's perhydrol in 100 c.c. of water), and 1 c.c. of 5 per cent. barium benzene sulphonate solution are placed in the small Peligot tube, and 0·5 c.c. each of the peroxide and sulphonate in the guard tube. The apparatus is then swept clear of air by a current of carbon dioxide. Ten grammes of the sample are added to the flask, and the contents heated to boiling within one minute, carbon dioxide being passed through the solution. The flame is lowered slightly and boiling is continued for ten minutes. In the case of dried fruits the time is extended to fifteen minutes. If no precipitate is obtained in three minutes from the time of boiling, sulphur dioxide is definitely absent. The water is then run out of the condenser, but the Peligot tube is not disconnected till the top of the condenser becomes too hot to hold. The end of the delivery tube is washed rapidly, and the mixed turbid solutions diluted and filtered into a Nessler glass. The filtrate and washings should measure about 70 c.c.

Four c.c. of hydrogen peroxide are introduced into a similar Nessler glass, and a current of carbon dioxide is passed through the liquid for about one minute. Water is then added to bring the volume to about 70 c.c., and 2 c.c. of the indicator (0·01 per cent. brom-phenol blue) added to each glass. The benzene sulphonic acid is titrated with $N/50$ sodium hydroxide solution till nearly neutral, when the contents of both glasses are diluted to the 100 c.c. mark, and the titration continued till the colours match. The titration can be carried out in artificial light.

The concentration of hydrogen peroxide and the details of procedure must be strictly adhered to if accurate results are to be obtained. The amount of hydrogen peroxide may be increased slightly if it is required to form a seal in the Peligot tube, provided that the same amount is used in preparing the control. In certain cases slight modifications are essential. Liquids are measured into the empty flask, and the acid added by means of a tapped funnel. Starches (10 grms.) are made into a paste with de-aerated water before being put into the flask, which,

after connection with the condenser, is heated and shaken until the mass thickens. The flame is then removed and agitation continued till liquefaction occurs, after which it is replaced and boiling continued. In the following table of results obtained, the sulphur dioxide present is that found by Monier-Williams' volumetric method:

	Nature of sample.	Amount used. Grms.	Titration, $N/50$. c.c.	Sulphur dioxide, parts per million. Found.	Present.
1.	Sausages	10	1·70	109	107
2.	Sausages	10	5·35 5·40	342 345	341
3.	Mince	10	0·65	41	43
4.	Mince	10	7·70 7·60	492 486	485
5.	Potted meat ..	10	0·10	6	9
6.	Soft sugar	10	0·90	57	57
7.	Gelatin	5	5·05	646	656
8.	Sultanas	10	7·35	470	480
9.	Prunes	10	0·15	10	10
10.	Raspberry pulp ..	16	8·45 $N/20$	859	873
11.	Dried apples ..	5	0·20	26	29
12.	Dried apricots ..	5	13·30	1702	1722

It was found that acetic acid, higher fatty acids, onions, mustard, nutmeg, and hydrogen sulphide do not interfere, and in no case did acidity or turbidity develop independently in the hydrogen peroxide. As a determination can be completed in 15 to 20 minutes with reasonable accuracy, the use of the test in the case of informal samples effects a considerable saving in time and materials.

I am indebted to Mr. F. W. Harris, F.I.C., for permission to publish the results of this investigation.

MAGNUS HERD.

CORPORATION CHEMICAL DEPARTMENT,
GLASGOW.

PHENOLS IN STERILISED MILK.

DURING the summer of 1929 numerous samples of commercial sterilised milk having an objectionable flavour and smell have been received at this Institute.

The flavour and smell were strongly suggestive of phenols, and in many samples were so marked as to cause buyers of the milk to threaten to submit samples to the Public Analyst in the belief that "carbolic acid" had been added as a preservative.

The flavour and smell were exactly reproduced in fresh milk by the addition of traces of *p*-cresol. It was therefore decided to try and show the presence of phenols in the samples of milk received.

About 500 c.c. of the tainted milk were steam-distilled until 100 c.c. of distillate had collected. The distillate was tested as follows according to the method described by Bell (*J. Inf. Dis.*, 1921, **29**, 424) for the detection of phenols produced by bacteria:

(A) A mixture of 0·1 grm. of *p*-nitraniline and 0·6 c.c. of pure concentrated hydrochloric acid were heated together for 10 minutes at 90° C. The mixture was made up, after cooling, to 5 c.c. with distilled water, 1 c.c. of $M/1$ sodium nitrite solution added, and the mixture heated to complete diazotisation.

(B) To the above steam-distillate, made alkaline with sodium carbonate, 6 drops of the *p*-nitraniline diazonium hydrate (A) were added.

A deep yellowish red colour resulted, indicating the presence of *p*-cresol.

The distillates from milk sterilised in the laboratory and from untainted commercial samples yielded negative results, and gave only the clear yellow colour of *p*-nitraniline-diazonium-hydrate.

Traces of *p*-cresol, added to freshly sterilised milk, gave, on steam-distillation, a colour exactly comparable with that produced by the distillate from tainted samples received in the laboratory.

On microscopical examination all the tainted samples were found to contain slender granulated bacilli which, presumably as spores, must have survived the heating process at 105° C. for 20 minutes.

A culture of this organism, isolated by Miss E. R. Hiscox, who has proved it to be a spore former, was inoculated into sterilised milk, and yielded, after 5 days' incubation at room temperature, on steam-distillation and addition of the reagent, a colour exactly comparable with that produced by *p*-cresol itself. Un-inoculated sterilised milk gave negative results.

According to Bell (*J. Inf. Dis.*, 1921, **29**, 424) *p*-cresol is derived from the bacterial degradation of tyrosine which can yield either *p*-cresol or phenol. In this case the degradation is due to spore-forming organisms which resist sterilisation.

This note is published in order to draw attention to the fact that phenols may be present in milk in quantity sufficient to render it unfit for consumption on account of the taste, and to point out that their presence in milk is not necessarily indicative of fraudulent additions.

A. T. R. MATTICK.

NATIONAL INSTITUTE FOR RESEARCH IN DAIRYING,
THE UNIVERSITY, READING.

Notes from the Reports of Public Analysts.

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

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1929.

OF the 1137 samples submitted under the Food and Drugs Acts, 78 were bought formally and 1059 informally. Forty-six were reported to be adulterated or incorrect.

"DIGESTIVE TEA."—A sample of so-called "Digestive Tea" bore on the label a statement that it was "free from crude tannin found in all ordinary tea," and therefore good for indigestion, gastritis, etc.

The advertisements connected with it claimed that it actually cured indigestion. The percentage of tannin found was 12·5, which is an average figure for Indian teas and actually higher than for many. The label is, therefore, a false

one. The packers were communicated with by the Medical Officer, and the matter was submitted to a meeting of directors. As the result of subsequent interviews, the firm agreed to introduce new labels on which all mention of tannin is omitted.

COLLODIUM FLEXILE.—This was a sample taken from the stock at the Broad Street Tuberculosis Dispensary. It was labelled "B.P." but was not of B.P. composition. The B.P. article should contain 2 per cent. of pyroxylin, 4 per cent. of Canada turpentine and 2 per cent. of castor oil. This sample, while containing the correct amount of castor oil, was deficient to the extent of 75 per cent. in Canada turpentine, and contained 2·9 per cent. of pyroxylin. In view of the fact that the article served its purpose perfectly well, and that most of the foreign Pharmacopoeias do not include Canada turpentine in the formulae, no action was taken.

BORAX IN GROUND GINGER.—The sample contained 2 per cent. of borax, a most unusual adulteration. The probability is that its presence was due to carelessness on the part of the shopkeeper, since the firm owning the shop have ascertained that the ginger supplied to them by the wholesale dealer was perfectly genuine. A letter of caution was sent to the firm.

H. H. BAGNALL.

Legal Notes.

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

ANALYSIS OF MILK: EVIDENCE BY THE PUBLIC ANALYST'S ASSISTANT.

ON October 11, 1929, a farmer was summoned at the Norwich Police Court for selling milk adulterated with 17·25 per cent. of added water on August 27, and with 16·75 per cent. of added water on August 28.

Mr. H. des Forges, for the Corporation, said that even if the defendant could prove that the milk had not been interfered with from the time it left the cow until the sample was bought, the Bench would still have to consider another certificate which showed the results obtained with a sample of milk taken at the defendant's farm as soon as the cows had been milked. Would cows which gave very bad milk on the Tuesday and Wednesday of one week be capable of giving very good milk on the following Tuesday?

Mr. W. F. Greeves, chief assistant to the Public Analyst, was called to prove the certificates of the Public Analyst, who was abroad. In his opinion the milk was adulterated with added water in each case.

In cross-examination, he said that he made the actual analysis of this milk, and the Public Analyst worked out the results from his figures and signed the certificate. He had never given evidence in a milk case before.

Mr. des Forges said that the certificate was signed by Mr. Lincolne Sutton. He was the Public Analyst, and was satisfied, and that was sufficient.

Mr. C. B. Hill, solicitor for the defence, submitted, as a point of law, that the prosecution, to establish their case, must prove that the analysis of the milk in question was, in effect, made by the Public Analyst. They had it in evidence that

the Public Analyst did not have anything physically to do with the milk, but had worked out the figures of the analysis made by the last witness. Although, at first sight, the magistrates might not think this very important from a practical point of view, he submitted that it was of the utmost importance, because the person who analysed the milk ought to have the necessary qualifications for the purpose. If this kind of thing were permitted, it would be possible for a public analyst to let anyone do the analysis in these cases and then to sign the analysis from the results.*

After a long discussion the magistrates decided against the defence, and the hearing was continued.

The defendant and his men gave evidence to show that the milk had not been tampered with. During the week in question the cows were without cake, and the milk returned to its normal quality when the cake arrived.

The magistrates dismissed the cases.

* NOTE.—Bell, *The Sale of Food and Drugs Acts*, p. 53, writing on the question of *Analysis by Deputy*, says: "The analyst need not make the analysis, but may do so through his assistants. (*Bakewell* v. *Davis*, 1894, 1 Q.B., 296; 58 J.P., 228; L.J.M.C., 93; 69 L.T., 832.)"

The conclusion drawn by Bell from this judgment is not altogether warranted by the facts. The case was stated by the justices for the City of Birmingham, and was with regard to a sample of milk certified by the Public Analyst to be 22 per cent. deficient in fat. The Public Analyst, in his evidence, stated that the analysis was carried out under his supervision; that he was not present during the progress of some of the processes, but that the weighing of the parts and other material operations had been done by him or in his presence; and he gave evidence as to the constituent parts of the sample of milk.

Among the points of law for the opinion of the Court was:

"Was the analysis properly and legally made by the Public Analyst within the meaning of the Sale of Food and Drugs Act, 1875?"

The Judges were of opinion that the conviction was right, and, therefore, upheld the contention of the justices that the Public Analyst had analysed the sample within the meaning of the Act.

Analysis by deputy is explicitly sanctioned under Sec. 13 of the Fertilisers and Feeding Stuffs Act, 1926.—EDITOR.

BORIC ACID IN CAVIARE.

ON November 6, 1929, a Co-operative Society and a retail firm were each summoned at Bow Street Police Court for selling caviare containing boric acid, contrary to the Preservatives Regulations. A plea of guilty was entered in each case, and it was agreed that they should be heard together.

Mr. A. Davies, for the Westminster City Council, said that in the first case the amount of boric acid present was 0·28 per cent., or 19·6 grains per lb., and in the second case 0·25 per cent., or 17·5 grains per lb. It was not permissible to use any at all.

Mr. Beck, for the retail firm, said that the use of boric acid was prohibited in every article of food, but other preservatives were allowed in some classes of food. Unfortunately caviare was never thought of when the Regulations were made. For 30 years his clients had sold the caviare in the same form that they received it.

The Magistrate here asked what quantity of boric acid was permitted before the Regulations came into force, and was informed that the old Departmental Committee recommended that 17·5 grains per lb. should be allowed in sausages, but that in butter, margarine and cream the amount was 35 grains per lb.

Mr. Beck, continuing, said that unfortunately the use of boric acid was part of the process to prevent the caviare putrefying. His clients had been in communication with those who imported the article, and attempts were being made to discover a method by which the use of boric acid could be avoided, but so far, without success. The result was that caviare, which had been imported in fairly large quantities from Russia, could not be sold at all in this country. It could be preserved to some extent by means of salt, but this made it unpalatable, and would ruin its sale in this country. It should be recognised that this was a seasonal trade, for the caviare was collected in the spring, and had to last the whole season. The amount of boric acid used was considered sufficient to preserve it for a reasonable commercial period.

Mr. Smith, for the Co-operative Society, said that his case was even stronger. The Society had never stocked caviare, but when it was ordered they obtained a supply from a neighbouring store. The Inspector who purchased the sample was asked to wait while it was sent for. Hitherto the Society had always received a guarantee with every purchase, but in this instance they omitted to obtain one; it was a piece of bad luck. It had never been discovered before that the sale of caviare involved an offence. If these prosecutions were to go on caviare could not be sold in this country, except in brine form.

The Magistrate said that it was common ground that the caviare was sold in circumstances absolutely forbidden by the Act. It was also common ground that the amount of boric acid used in these cases was not seriously injurious to health. This was the first time it had struck anyone to examine caviare for the presence of boric acid. In the circumstances he did not think that he ought to convict either of the defendants. He dismissed both summonses, but ordered the Co-operative Society to pay £3 3s. costs, and the retail firm £5 5s. costs.

On November 7 a Piccadilly firm was summoned by the Westminster City Council, at Marlborough Street, for a similar offence, the caviare in this case containing 0·18 per cent. of boric acid.

Mr. Walter Frampton, for the defence, pleaded guilty. He said that three summonses had been taken out against the firm, two of which had come before Mr. Fry at Bow Street, and he, after hearing the facts, and having regard to the reputation of the firm, had decided that justice would be met by the costs being paid. As this case was adjourned pending the hearing at Bow Street, he asked Mr. Dummett to take the same course.

The Magistrate said that he must show consistency in dispensing justice, and dismissed the summons under the Probation of Offenders Act, on payment of £3 3s. costs.

DIABETIC FLOUR.

On October 11th, 1929, a firm of millers was summoned at Salford for supplying flour not of the quality and substance demanded.

Mr. W. H. Robinson, Deputy Town Clerk, said that the inspector had obtained a sample of flour (which it was alleged had been ordered from the defendants as diabetic flour) as it was being delivered to a Salford grocer. A portion of this flour had been analysed by the City Analyst, who certified: "This is not a diabetic flour, and consists entirely of wheat flour."

The inspector said that, at an interview, one of the defendant's officials informed him that they did not sell the flour as diabetic flour, but as a special whole flour. He admitted that the flour might have been ordered as diabetic flour, but

that they did not inform their customers that they had no diabetic flour. Customers, said the official, ordered this flour in many ways, and when they knew what was wanted they sent this flour. The grocer was selling this flour at 5d. per lb., when at that time the price for that class of flour was 2d. per lb.

In cross-examination, the inspector admitted that on the delivery note signed by the grocer were the words "Special whole flour," and that the official of the defendants told him that this flour was always sold under that name, although he was aware that it was being sold for diabetic subjects. They had 30 or 40 customers who asked for it.

The grocer, giving evidence, said that he ordered this flour from the defendants as diabetic flour, and sold it to meet the request of special customers, some of whom had told him that they had found it much better for them than ordinary flour. Had he known that it was ordinary wheat flour he would not have paid 61s. a sack for it.

Mr. Gorman, for the defendants, said that he had no case to answer. The charge against them was that they had delivered to the grocer something which was to his prejudice, but the grocer's evidence showed that that was not the position. To begin with, there had never been a delivery of diabetic flour to him. The delivery note, which was not an isolated one, described this as special whole flour, and previous orders had been delivered under this description.

There were decisions, said counsel, in which it had been ruled that if, before the completion of a transaction, there was brought to the notice of a person receiving what in fact he was receiving, it was not to his prejudice, and in this case the purchaser, before he actually took delivery, signed the note for the special whole flour.

Mr. Robinson, for the prosecution, replied that the defendants were charged with selling an article of food not of the nature, substance and quality demanded. The purchaser did not get that article. He had ordered diabetic flour, and diabetic flour should contain considerably less starch and more gluten than whole flour. There was evidence that this was, in fact, whole flour, and therefore could not be diabetic flour. He therefore submitted that the purchaser was prejudiced.

The Stipendiary said that he did not think so, and dismissed the summons against the millers.

A summons against the grocer was then heard for selling to the inspector's agent 3 lb. of diabetic flour, for which 1s. 3d. was paid.

Mr. Leigh, for the defendant, contended that the flour was not sold to the prejudice of the purchaser. The sale of this article had increased through customers recommending it to their friends, who asked for the flour and knew what they were going to get.

The Stipendiary imposed a fine of £5, and said that the defendant must not sell this flour again as diabetic flour.

REMOVAL OF IDENTIFICATION MARKS FROM EGGS: COURT DEMONSTRATION.

On December 11, 1929, a Glasgow tradesman was convicted at the Glasgow Central Police Court of an offence under the Merchandise Marks Act of having sold, as eggs from the North of Ireland, foreign eggs from which the identification mark was removed.

Evidence was given by two food inspectors that they had found a man engaged in selling eggs from door to door, and purchased half-a-dozen from him,

having a notion that they were eggs from which the foreign identification marks had been removed. The man had stated that he was selling the eggs on behalf of the defendant.

Mr. T. Cockburn, F.I.C., Chief Assistant to the Public Analyst for Glasgow, to whom the six eggs had been sent, gave evidence that, by the use of ultra-violet rays, he had found that certain marks had been removed from the eggs by means of some corrosive substance. He demonstrated to the Court the way in which ultra-violet rays indicated that the shells of the eggs had been affected by treatment with a corrosive substance.

The defendant, giving evidence, said that he bought only North of Ireland eggs, and that, so far as he was concerned, there had been no tampering with them.

He was fined £5, the maximum penalty, with £2 costs.

Parliamentary Notes.

ACTION BY PRIVATE INDIVIDUALS UNDER THE ARTIFICIAL CREAM ACT.

ON November 14, 1929, the Minister of Health was asked by Mr. Lowther if his attention had been called to a case heard at Marlborough Police Court on July 2 and 12, and the subsequent appeal to the London Sessions on September 13 (see ANALYST, 1929, **54**, 542, 594). It was there decided that the Artificial Cream Act was not applicable, since the case had not been brought by a local authority but by an outside authority; and the Minister was therefore asked whether he was prepared to introduce legislation empowering individuals to seek protection under the said Act, when County or Borough Councils fail to carry out their statutory duties.

Mr. Greenwood, replying, said that he was aware of the proceedings referred to, but that he could not undertake to introduce amending legislation at the present time.

LABELLING OF CHEESE.

THE Minister of Agriculture was asked by Sir Charles Cayzer, on November 14, whether, in view of the fact that the Cheshire County Council had strongly urged that action should be taken by the Ministry of Agriculture and the Ministry of Health to ensure, by special legislation or otherwise, that cheese other than full-meat cheese should not be offered for sale unless it was clearly labelled or marked in such a way that the purchaser was made aware of its quality, he would now consider the desirability of introducing fresh legislation on the subject.

Dr. Addison (Parliamentary Secretary) replied that the question of the sale of half-meat cheese had been constantly before the Department for several years past; and he was not sure whether the hon. member was aware that local authorities already had the power under the Food and Drugs (Adulteration) Act, 1928, to deal with cases where such cheese was sold under a name indicating that it was whole-meat cheese, and that from time to time convictions had been obtained. Further legislation might needlessly harass the trader without commensurate advantage.

Ministry of Health.

SALE OF FOOD AND DRUGS ACT.

EXTRACTS FROM THE ANNUAL REPORT FOR 1928–1929, AND ABSTRACT OF REPORTS OF PUBLIC ANALYSTS FOR THE YEAR 1928.*

A TOTAL of 129,034 samples (an increase of 4770 over 1927) was reported upon by Public Analysts in England and Wales in 1928, and 7524 were adulterated or not up to standard, a slight increase on 1927. Apart from milk, the percentage of adulteration decreased from 3·9 to 3·2.

PRESERVATIVES.—There were 758 contraventions of the Regulations, of which 375 related to samples of sausages and meat products. Other foods included butter, cream, barley, cakes, cordials, fruit juices and confectionery. Nine preservative substances either had an excess or deficiency of the sulphur dioxide declared.

MILK, ETC.—Of 67,350 samples, 5542 (8·2 per cent.) were reported against (6·9 in 1927), but it is doubtful if this represents a real increase in the practice of adulteration. In 14 cases annatto had been added, often in conjunction with water; dirt was excessive in 52 samples, and preservatives had been added in 6 instances. Nineteen of 1195 samples of condensed, and 7 of 228 of dried, milks were chiefly deficient in fat.

CREAM.—This is the first year that preservatives have been prohibited, but the samples reported against were fewer than under the old Regulations. Boron was present in 55 of the total 2671 samples examined, 10 were deficient in fat or contained excess of water, and 5 were reconstituted or artificial cream.

BUTTER AND MARGARINE.—Of 10,544 samples of butter, 264 were reported against, the increase being due to the operation of the Preservatives Regulations. Foreign fats were present in 42 samples, excess of water in 92, and preservatives in 130; and in 12 of 46 samples of "bread and butter," the fat was margarine fat. Of 3720 samples of margarine, 28 contained excess of water, and 6 preservatives, and 14 infringed the labelling regulations.

LARD AND OTHER FATS.— Two of 2918 lards; 9 of 431 drippings; and 23 of 207 suets were adulterated. One lard was wholly fat not lard, and one contained water. Three samples of dripping contained free fatty acids, one boric acid, 2 water and 3 paraffin wax. Excess of rice flour or starch was present in 23 suets.

CHEESE.—Of 1333 samples of cheese, 18 "Cheshire cheeses" were reported as having been made from milk partly deprived of its fat, and 6 cream cheeses were ordinary milk cheeses.

BREAD AND FLOUR.—Five of 595 samples of flour, and 6 of 736 self-raising flours, were reported against. One sample of flour contained a considerable amount of fungus and 2 samples of egg flour consisted of self-raising flour and coloured maize.

JAMS AND MARMALADE.—Of 1584 samples, 41 were reported against—12 for excess of preservative, and the others for pectin preparations or fruit juices not declared on the label. A sample of raspberry jam contained foreign fruit pulp.

* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 1s. 6d. net.

VINEGAR.—A deficiency of acetic acid or substitution of artificial for malt vinegar occurred in 154 of 1904 samples.

SPIRITS AND BEER.—Of 2018 samples of spirits, 168 were adulterated, as were 13 of 485 beers. One bottled beer was contaminated with petroleum or paraffin oil, and another with a coal-tar disinfectant.

MISCELLANEOUS ARTICLES OF FOOD.—Fifteen coffee samples of 1580 were adulterated with chicory; 26 of 864 sweets and confectionery mostly contained excess of sulphites or talc; 28 baking powders (of 772) contained traces of arsenic or were deficient in carbon dioxide; 3 barleys were faced with talc or some other mineral, and 2 were stated to be infected with acari; 264 of 3069 samples of sausages, polonies, etc., mostly infringed the Preservatives Regulations; 52 of 1269 rices had excess of talc; copper was present in 1 sample of tinned peas, in 1 of tinned beans and 2 of pickles; tin was present in 25 samples of tinned fruit, fish and soup.

DRUGS.—Of 131 different kinds of drugs, 4703 samples were examined, and 262 were adulterated. Three samples of almond oil were composed of peach-kernel or apricot-kernel oil, and a sample of cod-liver oil tablets contained no cod-liver oil.

D. G. H.

Ministry of Agriculture and Fisheries.

THE following Regulations have been issued by the Minister of Agriculture and Fisheries:

AGRICULTURAL PRODUCE (GRADING AND MARKING) (EGGS) REGULATIONS, 1928. (Statutory Rules and Orders, 1928, No. 984.) H.M. Stationery Office. Price 1d.

AGRICULTURAL PRODUCE (GRADING AND MARKING) (APPLES AND PEARS) REGULATIONS, 1929. (Statutory Rules and Orders, 1929, No. 497.) Price 1d.

AGRICULTURAL PRODUCE (GRADING AND MARKING (BROCCOLI) REGULATIONS, 1929. (Statutory Rules and Orders, 1929, No. 201.) Price 1d.

AGRICULTURAL PRODUCE (GRADING AND MARKING) (TOMATOES AND CUCUMBERS) REGULATIONS, 1929. (Statutory Rules and Orders, 1929, No. 350.) Price 1d.

AGRICULTURAL PRODUCE (GRADING AND MARKING) (BEEF) REGULATIONS, 1929. (Statutory Rules and Orders, 1929, No. 812.) Price 1d.

AGRICULTURAL PRODUCE (GRADING AND MARKING) (WHEAT FLOUR) REGULATIONS, 1929. (Statutory Rules and Orders, 1929, No. 753.) Price 1d.

This Order states that the flour shall be made from sound, well-cleaned wheat grown in England and Wales. All-English (plain) flour to comprise the flours obtained from the wheat, provided that the ash content, as ascertained in a muffle furnace, shall not exceed 0·55 per cent., by weight, of the total flour. It shall be sound, free from taint or objectionable flavour, of good keeping quality and unbleached by artificial means, and free from all added chemical substances.

All-English (self-raising) flour to comprise all the flours obtainable from the wheat, provided that before the addition of any ingredients mentioned below, the ash content of the flour, as ascertained in a muffle furnace, shall not exceed 0·55 per cent., by weight, of the total flour. It shall be sound, free from taint or objectionable flavour, of good keeping quality and unbleached

by artificial means. It may contain such ingredients or mixture of ingredients as may be required to make the flour self-raising, subject to the Regulations for the time being in force in the Bread Acts (Amendment Act), 1922.

All-English (Yeoman) flour to be made exclusively from sound, well-cleaned wheat of "yeoman" varieties grown in England and Wales, the flour to comprise all the flours obtainable from the wheat, provided that the ash content, as ascertained in a muffle furnace, shall not exceed 0·55 per cent., by weight, of the total flour. It shall be sound, free from taint or objectionable flavour, of good keeping quality and unbleached by artificial means. It shall be free from all added chemical substances.

Department of Scientific and Industrial Research.

WATER POLLUTION RESEARCH.

WATER SOFTENING.

THE BASE EXCHANGE OR ZEOLITE PROCESS.*

THIS publication comprises a brief historical introduction to the subject, together with a summary of existing knowledge and a bibliography.

As distinct from the lime-soda process, in which lime and soda ash are used to soften water by precipitation of calcium as carbonate and magnesium as hydroxide, the base-exchange process utilises the reaction, $Na_2O,Al_2O_3,xSiO_2,yH_2O + CaCl_2 \rightleftharpoons CaO,Al_2O_3,xSiO_2,yH_2O + 2NaCl$. The metal combined with the aluminosilicate radical is thus replaceable reversibly by another metal, and the calcium and magnesium ions of hard water are replaced by sodium when the water is passed through a bed of such material. The spent material may subsequently be regenerated with brine.

A zeolite, strictly speaking, is a member of a group of naturally-occurring minerals which have the property of base-exchange, but the term is frequently used to apply to all base-exchanging materials. Certain of these natural silicates (*e.g.* potash green sands) are also used as fertilisers.

TECHNIQUE.—Hard water is fed in at the top of a closed, usually vertical, steel cylinder, 2 to 20 feet long according to the capacity of the plant, and lined with a bitumen enamel. The water is distributed over the active material, which occupies about one-half of the volume of the softener, and is sometimes supported on a bed of shingle, and collecting pipes at the base of the cylinder serve to remove the softened product. In some cases the water flows upwards, and this is preferable so long as channels are not produced in the material, since the whole bed is lifted, its resistance to flow thus decreased, and the loss of head therefore lessened.

Back-washing is employed before regeneration in order to remove any layers of dirt and to rearrange the zeolite particles, and is followed by treatment with 5 or 10 per cent. brine forced in at the bottom, or allowed to percolate from the

* Technical Paper No. 1, by A. R. Martin. Department of Scientific and Industrial Research, 1929. Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 6d. net.

top for from 5 to 20 minutes, and always in a reverse direction to the normal flow of water. The bed is not allowed to drain on account of the inclusion of air-bubbles, but is washed with hard water for 15 minutes, when zero-hardness should again be obtained. In the salt-recovery process the spent brine is used for the first stage of the next regeneration.

The exchange-value of a material is the weight in lbs. (or grains) of the equivalent quantity of CaO removed by 100 lbs. (or 1 cubic ft.) of material, when hard water is passed through under specified conditions until it just ceases to be of zero hardness. The value depends on the depth and particle size of the bed, the rate of flow and the amount of salt used for regeneration (usually about 6 times the weight of CaO equivalent to the alkaline earth metal absorbed).

ADVANTAGES AND DISADVANTAGES.—Advantages of this process over the lime-soda process are:—(1) Zero hardness is attainable, whilst the lime-soda process gives a hardness of at least 2°. (2) The process automatically adjusts itself to variations in hardness of the supply. (3) There are no difficulties of coagulation and disposal of a precipitate. (4) The process may be operated under pressure. (5) The apparatus has no moving parts, and occupies relatively little space. (6) The process is cheaper for permanent hardness, though dearer for temporary hardness, capital expenditure being about the same for both processes.

Advantages of the lime soda-process are:—(1) There is no increase in total solids as only the theoretical quantity of reagent is added. (2) It may be used for turbid, ferruginous or acid waters, which may inactivate the zeolite layer by the formation of an impermeable layer or, with acid water, by the irreversible substitution of hydrogen for sodium. (3) There is no loss of activity or of material by disintegration or solution. This is most marked with artificial zeolites.

Combinations of both processes are also used, though every case should be considered on its own merits. Thus, for high pressure boiler-feed water of zero hardness the combined process is recommended in preference to the base exchange process alone, which may give rise to foaming, priming, corrosion, and caustic embrittlement owing to the formation of caustic soda and carbon dioxide from the sodium bicarbonate which remains after removal of the temporary hardness. The American Society of Mechanical Engineers advise 1, 2 and 3 for the ratios of sodium sulphate to total alkalinity (as Na_2CO_3) in the feed-water for boiler-pressures of below 150 lbs., 150 to 250 lbs., and above 250 lbs. per square in., respectively, in order to prevent embrittlement, and these ratios may be attained by addition of sulphuric acid.

For drinking water the base-exchange process has the advantage of simplicity, and it is also used for water required in the textile, dyeing and laundering industries, either alone or combined with the lime-soda process.

PREPARATION OF THE SILICATES.—Originally kaolin, quartz and soda ash were fused together, and the product leached with hot water. A superior product is now obtained at lower cost either by precipitation of sodium aluminate with sodium silicate in solution below 20° C., or by peptisation of certain natural greensands (*e.g.* glauconite) or clays. In the former case a gel is obtained which is dried at 80° C., or the precipitate is flocculated with sodium sulphate, and the product yields an alkaline water for some time. In the latter, the mineral may be soaked in a solution of sodium silicate containing aluminium sulphate. Synthetic zeolites have the greater exchange values, but the greensands give more robust beds, which will resist even acid- or heat-cleansing treatment.

CONSTITUTION.—There is evidence for the general formula $M_2O,Al_2O_3,nSiO_2,(n-1)\ H_2O$, for the active silicates, where M is an alkali metal and n is 3, 4 or 5. For the inactive silicates the formula is $M_2O,Al_2O_3,nSiO_2,(n+1)\ H_2O$,

where n is 3 or 4. Structural formulae have also been suggested, but are regarded as speculative, though there is good reason to believe that in the active silicates M must be united through oxygen to aluminium and not to silicon.

Some of the water may be removed at moderately high temperatures or by desiccation; and, though there is some doubt on the matter, it is usually supposed that 3 molecules of water are present as water of crystallisation and 2 as water of constitution. The principal evidence for the theory that zeolites are gels, in which the water is held in an aluminosilicate network, is based on the vapour pressure-water content curves, on the adsorptive power of the dehydrated gel, and on the high electrical conductivities of the zeolites. Thus, the specific conductivities at 20° C. are 6×10^{-4}, 1×10^{-4} and 2×10^{-3} reciprocal ohms, for the zeolites of silver and the alkali metals, of the alkaline earths, and of the trivalent metals, respectively (Günther-Schulze, *Z. Elektrochem.*, 1919, **25**, 330; 1920, **26**, 472; 1921, **27**, 292, 402). The volume of the pores is estimated at about 30 per cent. of the total volume (*i.e.* solid plus pores).

THEORY OF BASE EXCHANGE.—Base exchange never proceeds to completion, and, according to one school, the equilibrium is governed by the law of mass action, whilst another maintains that it is due to exchange adsorption, *i.e.* equivalent amounts of cations are adsorbed from the salt solution and expelled from the aluminosilicic acid gel. The velocity of the base-exchange reaction is rapid, and no anions are involved.

The evidence for both theories is summarised, but enables no definite conclusion to be drawn. The fact that the Freundlich isotherm may be applied (Wiegner and Jenny, *Koll. Zeit.*, 1927, **42**, 268) does, however, give a favourable bias to the adsorption theory.

J. G.

Government of Palestine.

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1928.

IN his Annual Report to the Department of Health the Government Analyst, Mr. G. Baker, F.I.C., states that samples to the number of 6738 have been examined for various Government Departments, as against 5620 in 1927. The amount of advisory work has increased considerably.

MILK.—Of the 4133 samples of milk examined for the Department of Health in the fourteen centres equipped for milk testing, 3546 were taken from street vendors and the remainder from daily supplies to hospitals. Prosecutions for watering or skimming were instituted in 152 cases, or 3·7 per cent., compared with 4·4 per cent. in 1927.

SACCHARIN.—The prohibition of the use of saccharin and other sugar substitutes in local mineral water factories has entailed the examination of 185 samples for the presence of such sweetening agents, in addition to the routine examination for lead. Saccharin was found in two samples.

SEMNEH.—The sale of adulterated semneh and edible oils still appears to be a profitable enterprise, notwithstanding a considerable number of prosecutions. Of 503 samples examined, 27 per cent. were grossly adulterated. Much of the adulterated semneh is imported, and in some cases it has been possible to return large consignments to the country of origin on the results of analysis of samples

taken in Customs. This entails some delay and inconvenience to trade, but when it can be adopted it is probably the best means of control.

OLIVE OIL.—The usual adulterant of olive oil is cottonseed oil, but the use of a pure mineral oil ("Vaseline oil") as an adulterant appears to be gaining favour. In this connection it has been ascertained that the representative of a foreign firm of mineral oil manufacturers has recently spent some time in Palestine endeavouring to do business with local oil producers.

Two consignments of such mineral oil coloured a greenish yellow were detected by the analysis of samples taken in the Customs, and a sample of so-called olive oil from Egypt contained 75 per cent. of mineral oil, the remaining 25 per cent. being olive oil of high acidity, which gave it an "olive" flavour.

Imported soya bean oil is now in competition with the indigenous oils, and will, presumably, provide another means of adulteration.

LEGAL, JUDICIAL AND POLICE DEPARTMENTS.—The services of these laboratories continue to be used to an increasing extent by those responsible for criminal investigation, and the policy has been to encourage such use. Some relief from the obligation to attend the courts to give verbal evidence is provided by the Criminal Procedure (Evidence) Ordinance, 1927, under which the certificate of the Government Analyst or of the Officer in charge of the Laboratory is admissible as evidence. In criminal assize cases, however, the court still demands verbal evidence in many instances.

BLOOD STAINS.—The examination of alleged blood stains has shown that, among other things, fruit juices (especially that of the olive), ferruginous earth and faeces will often produce stains with a strong semblance of blood. In one such case, proof of the absence of blood and the presence of a saponifiable oil, tannin, and a purple-red vegetable colour in stains on a camel saddle gave support to the accused's declaration that he had carried olives and not a dismembered human body on his camel.

The use of alumina cream has been found advantageous in obtaining clear extracts of blood stains in obstinate cases without interfering with the precipitin test.

COUNTERFEIT COINS.—Following the introduction of the new Palestine currency, counterfeit coins have been much in evidence. Forty suspected coins have been submitted during the year, for laboratory examination, of which 34 were confirmed to be counterfeit. The outstanding features of most of the counterfeit coins are that they contain considerably more silver than the genuine currency, that they are cast, and that they are deficient in diameter to the extent of about 1/50 inch.

FORGED DOCUMENTS.—Five documents have been examined in connection with cases of alleged forgery. It is, perhaps, worthy of note that the common practice of signing on or across a row of adhesive revenue stamps on a document facilitates forgery, as there have been several instances where such stamps bearing the whole or greater part of the signature have been transferred to other documents.

Eleven saws have been submitted in connection with criminal damage to trees. By microscopical examination and the colour reactions of the tannins it has been possible to identify the wood fibres on the teeth of some of the saws.

In connection with the Dangerous Drugs Act, 23 specimens have been submitted for identification. The findings were:—Cocaine hydrochloride, 8; opium, 1; negative, 8; morphine hydrochloride, 1; and "hashish," 3.

In two instances the "hashish" was mixed with cocoa and sugar and moulded into large tablets. In many cases it appears that the investigating authorities find it possible to identify "hashish" without submitting samples for analysis.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

The Reaction of Borate and Sugars. II. Optical Activity of Sugars in Borax Solution and the Configuration of Mutarotatory Isomers. M. Levy and E. A. Doisy. (*J. Biol. Chem.*, 1929, **84**, 749–762.)—During a study of the effect of borate on the oxidation of sugars by the authors (*J. Biol. Chem.*, 1928, **77**, 733) attention was attracted to the investigations of the effect of borax on the optical activity of glucose and fructose, apparently first reported by Rimbach and Weber (*Z. physik. Chem.*, 1905, **51**, 477). These workers observed that the optical activities of these sugars were less (*i.e.* nearer 0°) in borax solutions than in distilled water, but that the values of the optical activities were normal in boric acid solutions. The results obtained on this subject by other workers are discussed. Measurements have now been made of the optical activities of sugars and certain derivatives in borax solution, and also a careful study of the effect of acidification has been made. The experimental data are discussed with respect to the formulation of the α,β-isomers of the sugars. Graphs and tables show the results obtained. It is definitely concluded that the optical activities of sugars differ in borax solution from the optical activities in water. The expected activity is restored when the base of the borax is neutralised by a strong acid. The acidified solutions undergo rotatory changes before reaching equilibrium, which can be correlated with the configuration of carbon atoms 1 and 2 of the aldehyde sugars. The data obtained have been used to show that the more dextrorotatory of the α- and β-isomers of each aldose sugar has the *d* configuration for the aldehydic carbon atom. The configurations given in a table agree with those adopted by Boeseken (*Ber.*, 1913, **46**, 2612), Boeseken, Kerstjens and Klamer (*Proc. Roy. Acad. Amsterdam*, 1916, **18**, 1654), and Boeseken and Couvert (*Rec. trav. chim. Pays-Bas*, 1921, **40**, 354) from conductivity data, except for mannose. The authors feel that the configuration presented by them for mannose is more reliable than Boeseken's configuration. In addition, their configuration is consistent with the generalisations of Hudson (*J. Amer. Chem. Soc.*, 1909, **31**, 66). P. H. P.

Composition of Neem Oil. The So-called Margosic Acid. A. C. Roy and S. Dutt. (*J. Soc. Chem. Ind.*, 1929, **48**, 333–335.)—The oil from *Melia Azadirachta*, the Indian neem or margosa seed, was investigated, particularly with regard to the chemical nature of the mixed fatty acids. By distilling the fatty acids under reduced pressure 3 fractions were obtained: a volatile portion boiling at 60–100° C., and consisting mainly of water and small quantities of butyric, valeric and hexoic acids; a major portion of palmitic, stearic and oleic acids with

a small quantity of linolic acid; and a small non-volatile residue consisting of unsaturated resinous acids with small quantities of arachidic and lignoceric acids. The so-called margosic acid, prepared according to Chatterjee and Sen's method (*Indian Med. Gaz.*, 1919, **54**, 174), was found to be impure oleic acid, since, on distillation in a high vacuum, it was resolved into oleic, linolic, and small quantities of higher and resinous acids. The unsaponifiable matter of the oil contained phytosterol. The composition of the fatty acids was as follows:—Lower fatty acids, 2·31; stearic, 21·38; palmitic, 12·62; oleic, 52·08; linolic, 2·12; arachidic and lignoceric, 0·74; and unsaturated resinous acids, 2·76 per cent. D. G. H.

Sterols of Cacao. H. Labbé, H. de Balsac and R. Lerat. (*Compt. rend.*, 1929, **189**, 864–866.)—To separate the unsaponifiable constituents, commercial cocoa butter is saponified in alcoholic solution by excess of sodium hydroxide in a reflux apparatus, a current of pure, dry carbon dioxide being passed into the flask at the end of the operation to saturate the excess of alkali and maintain an inert atmosphere, the substances to be isolated being readily oxidisable. The residual mass is mixed with sand, dried, granulated and extracted with ether, the solution obtained being dried and distilled to recover the ether. The remaining yellow paste of crude sterols is treated with petroleum spirit, almost pure α-sterol then separating as a crystalline precipitate, which is carefully dried. The portion soluble in the petroleum, after evaporation of the solvent, is again saponified with alcoholic potassium hydroxide, and the alcohol subsequently expelled in a current of carbon dioxide. The residue is dissolved in water and the solution extracted with ether, the mass left after expulsion of the ether being purified by crystallisation from either alcohol or an acetone-alcohol mixture: this represents a different sterol (β). An oily, uncrystallisable product, showing the sterol reaction, also remains. For cocoa butters of different origins, proportions of total sterols varying from 0·26 (Lomé) to 0·79 per cent. (Caraque) were found. The beans themselves contain from 0·2 to 0·35 per cent. of sterols, the germs very small proportions, and the husk from 2·35 to 3·32 per cent. (7·77 to 9·3 per cent. of the butter yielded). The two sterols occur in the same proportions in the different parts of the bean.

T. H. P.

Studies in Liquorice Root and Liquorice Extract. IV. New Substance in Chinese Liquorice Root. P. A. Houseman and C. K. Swift. (*Amer. J. Pharm.*, 1929, **101**, 679–687.)—A new substance, $C_{20}H_{21}O_9$, was prepared from Chinese liquorice root by extracting 10 kilos. of dried shredded root for 60 hours with 95 per cent. alcohol, treating the brown semi-solid residue with 10 litres of boiling water, boiling down to 3 litres, treating with another 4 litres of boiling water, and decanting the supernatant liquid at 80° C. from the soft resinous mass, which was given a second and third treatment with boiling water. On cooling, the clear liquid was decanted from the resin which settled, and the resin was boiled 3 times with water. From the 15 litres of aqueous extract there were obtained 27 grms. of crude crystals, which were purified by recrystallising from boiling water. The needle-shaped crystals melted at 202–204° C. (uncorr.), and had α_D in absolute

alcohol + 48·8°, and molecular weight 404 to 406 (cal. 405). Fifteen reactions are detailed, including the formation of picric acid with fuming nitric acid, acetylation, which gave 145 per cent. of a product melting at 165–170° C., showing the presence of 4 hydroxyl groups; and tests with sodium hydroxide, showing the absence of carboxyl groups and the phenolic character of the acid substance. From the alkaline or acid hydrolysis products yellow crystals were obtained, which were found to be closely related to hydroxy-α-lapachone, $C_{15}H_{14}O_4$ (m.pt. 187° C.).

D. G. H.

Microchemical Identification of *Artemisia Santonica*. F. Amelink. (*Pharm. Weekblad*, 1929, **66**, 1025–1028.)—If 50 mgrms. of the powdered sample are made into a paste with 4 *N* hydrochloric acid, the santonin may be extracted rapidly, and almost quantitatively, with chloroform (solubility 1 in 4·35) with the removal of only a little resin. The residue is sublimed between two microscope slides at an angle of 30°, and, on the addition of a drop of water or acid, well-formed, *d*-rotatory, colourless, right-angled prisms, 5 to 50μ long, are visible. Van Lindo's test, in which a red-purple colour is produced with warm dilute sulphuric acid (2 parts with 1 of water) made just yellow with ferric chloride, may then be applied, but is not specific. A special apparatus is described for the two operations, by means of which positive results were obtained with 10 mgrms. of sample containing 2·6 per cent. of santonin. J. G.

Quality Standard for Crocus. E. H. Wirth. (*Amer. J. Pharm.*, 1929, **101**, 716–724.)—The tinctorial power of crocus, due to hydrolysis of the glucoside crocin to crocetin, may be ascertained by taking 0·1 grm. of the powdered dried crocus (approximately 40), and making up to 100 c.c. with water, leaving at room temperature with frequent shaking for 3 hours, and filtering. One c.c. of the filtrate is diluted to 10 c.c. and compared in a colorimeter with a 0·01 *N* solution of potassium dichromate. A 1:10,000 solution of crocus thus prepared should show a depth of colour not less than that of an equal depth in mm. of a 0·01 *N* solution of potassium dichromate. In the samples studied, which all had a style percentage below 10, drying made no material difference to the test. Of samples purchased in local stores none fell below the above standard, and the average was 30 per cent. over the standard, which is approximately that of the 1905 Dutch Pharmacopoeia, and the German Pharmacopoeia of 1926. Experiments to determine the effect of light and age upon crocus have been begun, but light may be assumed to be an even greater factor than age in deterioration. The colours imparted by crocus to various solvents were investigated by comparison of solutions of 0·1 grm. powdered crocus in 50 c.c. of solvent; calculated for a 20 mm. depth of 0·001 *N* solution of potassium dichromate they gave depths in mm. as follows:—Ethyl alcohol, 0·12; methyl alcohol, 0·16; chloroform, 16·00; ether, 22·0; xylene, 40; benzene, 40; carbon tetrachloride, 50. D. G. H.

Use of the Antimony and Antimony Trioxide Electrode for Determination of the Dissociation Constants of Certain Local Anaesthetics and Related Compounds. F. Fenwick and E. Gilman. (*J. Biol. Chem.*, 1929,

84, 605–628.)—Roberts and Fenwick (*J. Amer. Chem. Soc.*, 1928, **50**, 2125) described the antimony and antimony trioxide electrode and its use as a measure of acidity in considerable detail. The discussion of the field of its applicability has now been extended to solutions of special interest to the biological chemist and pharmacologist, in which the use of the hydrogen electrode may be attended with difficulty or may yield erroneous results. Acidity determinations have been made at 25° C. with the antimony and antimony trioxide electrode on a series of solutions of four new local anaesthetics of the naphthalene series, first made in the same laboratory by Hill and Robinson (unpublished data), together with procaine, diethylaminoethanol and aniline hydrochloride. From these sets of values the corresponding basic dissociation constant was computed by an extrapolation involving the Debye-Hückel equation for the activity coefficient of an ion at vanishing concentration. This constant was compared in each case with the apparent dissociation constants calculated for the several dilutions measured. The order of increasing basicity of the four related anaesthetics proved to be the same as the order of increasing anaesthetic efficiency. The relationship between the order of increasing basicity and the chemical structure of the members of the naphthalene series was found to be the same as that discovered for the procaine series by Vliet and Adams (*J. Amer. Chem. Soc.*, 1926, **48**, 2158). Comparison measurements made with the antimony and hydrogen electrodes on solutions of the compounds named, and also benzoic acid and *p*-aminobenzoic acid failed to agree; the behaviour of the hydrogen electrode is shown to be erratic and untrustworthy. That there is a definite correlation between the efficiency of local anaesthetics of a *related series*, their basic dissociation constants and their chemical structure seems positive; possibly, any local anaesthetic, to be effective, must have a basic constant within a certain range of values. A determination of the constant should, therefore, prove a valuable aid in predicting the anaesthetic potency of a given compound and a guide to further synthesis. P. H. P.

Erratum.

Rapid Method for Quinine Determination. G. A. Sticht. (ANALYST, 1929, **54**, 607.)—For the sentence commencing "A solution of 6 grms. of citric acid . . . . . ," *read* "A solution of 2 grms. of citric acid in 10 c.c. of water is made slightly alkaline to phenolphthalein with sodium hydroxide solution, boiled, 4 grms. of citric acid added, and the mixture added to the hot extract . . . . . ."

Biochemical.

Titration Method for Blood Fat. J. L. Stoddard and P. E. Drury. (*J. Biol. Chem.*, 1929, **84**, 741–748.)—A method is described for the isolation and titration of the fatty acids. The blood is extracted with alcohol and ether, the extract saponified, the fatty acids separated, filtered, washed, dissolved in alcohol, and titrated, with phenol blue as an indicator. In the development of the method,

technical difficulties in the filtration and washing of the fatty acids were the chief obstacles. These were finally overcome by the technique of filtration through previously heated paper pulp mats in small Gooch crucibles, and by the use of salt solution for washing. In a series of 10 blood samples from normal fasting subjects the fatty acids averaged 294 mgrms. per 100 c.c. All but one ranged between 260 and 333; the exception was 237 mgrms. One other supposedly normal sample gave a figure of 193 mgrms. per 100 c.c. A method similar in general principle was described by Stewart and White (*Biochem. J.*, 1925, **19**, 840); in this method the fatty acids were not separated, washed, and titrated directly. The method of Stewart and White is criticised by the authors for the following reasons: (1) A very slight error in measurement of either the sodium hydroxide used for saponification or the hydrochloric acid used for neutralisation makes a very large per cent. error in the calculated blood fat. (2) In saponification the glass is attacked and sodium silicate formed, which interferes with the titration. (3) Carbon dioxide will be absorbed during titration unless special precautions are taken. In the new method the fatty acids are isolated and washed, and the only amounts of alkali which come into quantitative relations are those used in the direct titration of the fatty acids. Solution of the fatty acids in alcohol removes any silica which may have formed. Carbon dioxide is boiled off at a low P_H, and special precautions are taken to avoid absorption during titration. Much work was done on known mixtures of oleic, palmitic and stearic acids. Not more than 4 parts of oleic to 1 of palmitic or stearic can be filtered off and washed quantitatively. Pure fatty acid mixtures are more difficult to deal with than those derived from blood, partly because cholesterol is present in the blood extracts at the time of filtration, which makes a harder precipitate. In a series of various pathological blood samples none has been found that offers as much difficulty in filtration as the artificial mixtures, which, nevertheless, give accurate results. Addition of cholesterol to the artificial mixtures had no effect on the results. Tables give the results of test analyses. The presence of cholesterol during titration of the fatty acids does not affect the titration; neither does the presence of the fatty acids during cholesterol determination interfere with the colour reaction given by cholesterol. P. H. P.

Study of Glutathione. I. Preparation in Crystalline Form and Identification. E. C. Kendall, B. F. McKenzie and H. L. Mason. (*J. Biol. Chem.*, 1929, **84**, 657–674.)—The authors have investigated the preparation and identification of glutathione; a table shows the amounts of glutathione obtained from 47 lots (each of 45 kilos.) of bakers' yeast. The method of Hopkins (*Biochem. J.*, 1921, **15**, 286) for the isolation of glutathione from yeast has been modified as follows:—The suspension of yeast is extracted with cold water in the presence of benzene. The cells are removed in a large centrifuge. The solution is precipitated with neutral lead acetate. The P_H of the solution must be about 5·5. The lead precipitate is decomposed with sulphuric acid, and some impurities are removed by raising the P_H to 4·0 with barium hydroxide. The solution is made acid, and

is treated with phosphotungstic acid at 0° C. The phosphotungstic acid is removed with barium, and the glutathione is precipitated with mercury sulphate. The mercury precipitate is decomposed with hydrogen sulphide. Sulphuric acid is removed from the solution, which is then concentrated to a small volume. On standing, the solution sets to a crystalline mass, and the crystals are washed with glacial acetic acid and absolute alcohol, and re-crystallised from water. This material is a tripeptide of glutamic acid, glycine and cysteine. The glycine is attached to the carboxyl group of glutamic acid nearest to the amine group, and the cysteine is attached to the other carboxyl group. The chemical reactions used in the determination of the structure of the tripeptide are given. The material precipitated from the mother liquor of the crystals with absolute alcohol has nearly the same percentage composition, and glycine can be separated after hydrolysis from this material and from the crystalline tripeptide in about the same yield. It is probable that nearly all of the cysteine is present in the form of the tripeptide. The formula suggested for glutathione is based on three facts : (1) Succinic acid is obtained after hydrogen peroxide treatment only after hydrolysis. (2) Glycine but no glutamic acid can be separated after treatment with nitrous acid. (3) Neither glutamic acid nor glycine can be separated after oxidation with hydrogen peroxide. This last fact is negative in character, and therefore, until more positive evidence is obtained, the structure of the tripeptide must remain in doubt. The results obtained by Hopkins on the identification of glutathione leave no doubt that the substance which he isolated was glutamyl cysteine. The formation of this dipeptide from the tripeptide, glutathione (glutamyl-glycine-cysteine), is an obvious explanation of the source of the dipeptide. P. H. P.

Vitamin Content of Honey and Honeycomb. H. B. Kifer and H. E. Munse. (*J. Agric. Res.*, 1929, **39**, 355–366.)—Three samples of honey, representing extremes of colour variation, were used for the tests—a white clover honey from Ohio, a very dark buckwheat honey from New York State, and a white clover honey from Vermont. Vitamin *A* tests were made according to Sherman and Munsell's method (*J. Amer. Chem. Soc.*, 1925, **47**, 1639), but no indication of its presence was found in any of the honeys or in the honeycomb from the third sample (the only honeycomb tested). Vitamin *B*, tested for by Sherman and Spohn's method (ANALYST, 1924, **49**, 42) was also absent from the samples; vitamin *C*, tested for by Sherman, La Mer and Campbell's method (ANALYST, 1922, **47**, 216), was not present in any appreciable quantity; and with vitamin *D* tests, by Munsell and Black's method (*J. Amer. Pharm. Assoc.*, 1928, **17**, 139), all the honeys gave negative tests, and the rats had severe rickets. D. G. H.

Preparation and Properties of Vitamin *C* Concentrates from Lemon Juice. D. P. Grettie and C. G. King. (*J. Biol. Chem.*, 1929, **84**, 771–776.)—A new procedure is described for the concentration of vitamin *C* from lemon juice. Fractional precipitation of the active material is carried out with the use of lead salts, as indicated by the work of Zilva, and organic solvents. A valuable step

in the concentration is extraction with butyl alcohol. The observation that butyl alcohol extracted the yellow colour and wax from lemon juice led to a preliminary experiment to determine whether vitamin *C* was extracted by this means. During the decitration and precipitation procedure it had been found that the yellow colour was parallel with the active phase. Feeding experiments on guinea pigs showed that the butyl alcohol extraction failed to remove an appreciable amount of vitamin *C* from the water phase, but did remove approximately 0·33 mgrm. per c.c. of fatty material. Treatment of the vitamin *C* concentrate with ethyl alcohol and anhydrous hydrogen chloride, followed by distillation *in vacuo* (at 50° C. and 0·2 mm., and up to 250° C. and 0·03 mm.), gave no evidence of esterification or distillation of the antiscorbutic factor. There was very little loss in activity of the preparation after it had stood for 15 hours in a saturated alcoholic solution of hydrogen chloride at 25 to 50° C. It has been reported that vitamin *C* is insoluble in absolute acetone, but it was thought that it might be soluble from a more concentrated material than desiccated lemon juice. The results of an experiment show that the vitamin is definitely soluble in absolute acetone. An analysis of the absolute acetone extract obtained is given. P. H. P.

Value of Irradiated Milk. K. H. Coward. (*Lancet*, 1929, Nov. 23, 1090.)—Various samples of milk from the same source irradiated under different conditions have been found to contain varying amounts (from 0·2 to 2·0 units per grm.) of antirachitic activity (vitamin *D*). The unit of measurement is that adopted by the Pharmaceutical Society of Great Britain, *i.e.* the amount of antirachitic activity contained in 0·0001 mgrm. of the Society's standard preparation of irradiated ergosterol. The corresponding samples of untreated milk contained negligible amounts, or, at the most, 0·1 unit per grm. A sample of skimmed milk contained about half the vitamin activity of the whole milk from which it was obtained, when both had been irradiated under the same conditions. The antirachitic potency of irradiated milk is compared with that of cod-liver oil. It is shown that half a pint of irradiated milk with a potency of 0·2 unit per grm. contains 60 units of vitamin *D*, which is the amount contained in 0·6 grm., or 30 drops of a good average cod-liver oil. The following two conclusions are emphasised:—(1) Samples of irradiated milk vary enormously in antirachitic potency. Whilst the irradiation has produced a demonstrable increase of potency in all samples which have been examined, in comparison with the original untreated milk, the variations in the finished products show that there is an obvious risk that samples may be sold which have been treated ineffectively. (2) Ordinary milk sold throughout the greater part of the year contains hardly any antirachitic vitamin.
P. H. P.

White and Brown Bread. R. McCarrison. (*Brit. Med. J.*, Nov. 16, 1929, 913–914.)—In the towns and cities of India, the use of white bread is increasing, whilst that of the unleavened bread made by the people themselves from freshly ground whole wheat is declining. To ascertain the relative dietetic values of the two, a series of experiments has been made on twenty-six groups, each of three male

and three female rats, great care being taken to ensure identical conditions in all cases and to avoid incidental errors. The two flours were made up with water into cakes of unleavened bread and then lightly cooked on an iron plate over an open fire in the customary Indian manner. The bread formed the basal diet, various supplements being supplied in the different experiments. Progressive measurements of the body weight showed that, in every instance but one, whole wheat flour was superior to white flour. The sole exception occurred when the animals were supplied with as much whole milk as they cared to drink (an average of 20 c.c. per day), together with 5 per cent. of dried yeast; identical results were then obtained with the two kinds of bread.

Moreover, whole-wheat unleavened bread, although made from inferior wheat, proved superior to baker's white bread, so that the yeast used (about 2 per cent.) did not supply the deficiency of the white flour. The pernicious effect of vegetable margarine (cocogem) is clearly brought out by the experimental results, and emphasis is laid on the fact that, when the diet contains a considerable amount of fat, as either margarine or butter, it is essential for the vitamin *B* content of the food to be proportionate to the amount of fat, growth being otherwise retarded.

T. H. P.

Bacteriological.

New Species of Oidium. A. Chaston Chapman. (*Trans. Brit. Mycol. Soc.*, 1929, **14**, 291–293.)—This mould was found as a hard gelatinous or tough leathery mass in a main sewer just beyond the entry of a factory sewer conveying a faintly acid effluent containing about 1 grm. of total dissolved matter per 100 c.c.—this being mainly sodium acetate and sodium sulphate—but being devoid of carbohydrate and nitrogen. The organism resembles *Oidium matalense*, isolated by Castellani in 1915, but appears to be either a different variety of this or possibly a different species. It is strictly aerobic and grows readily on malt wort, sterile milk, glucose or lactose broth, Raulin's solution, or nutrient gelatine (no liquefaction), but not in fermented malt wort. In the factory effluent alone it develops very slowly, but addition of a little nitrogen in the form of sterilised domestic sewage results in very rapid growth. T. H. P.

Standardisation of the Strength of the Organism (Bacterium C) used in the Chapman Biological Method for the Determination of the Preservative Power of Hops. A. Chaston Chapman. (*J. Inst. Brew.*, 1929, **35**, 363.)—The uncertainty arising from possible variations in the activity of this organism (*ibid.*, 1925, **31**, 13) is removed as a result of the experiments here described. Quantities varying from 0·5 to 2·5 c.c. of a 1 per cent. solution of pure phenol in water were measured into a series of test-tubes, the volume being made up in each tube to 10 c.c. with nutrient agar. The tubes were then heated for 10 minutes in a steam steriliser, cooled to 40° C., and inoculated with 3 drops of an 18-hour broth culture of the organism grown at 37° C. The tubes were next shaken, and the contents poured into Petri dishes, allowed to set, and incubated at 37° C. for

48 hours, the appearance being noted. Remarkably constant end-points were thus obtained, the organism growing freely on the 1·5 c.c. phenol plate, but not at all on the 2 c.c. plate. The same end-point was obtained with different sub-cultures of the original strain, including one several years old. The constant virility of the organism thus seems to be established. T. H. P.

Significance in Oysters and Water of Aerobic Non-Sporulating Bacteria producing Gas from Lactose. C. A. Perry. (*Amer. J. Hyg.*, 1929, **10**, 580–613.)—From eosin and methylene-blue agar plates made from stool specimens from 56 persons, 112 cultures of lactose-fermenters have been obtained, 83 per cent. of such cultures giving an acid reaction to methyl red and a negative Voges-Proskauer test; of these 90·3 per cent. proved to be *B. coli*. In estimating potentially dangerous faecal pollution of water and oysters, the presence or absence of *B. coli* should be the basis for judging the sanitary condition of these products. Practically all samples of water and oysters contain a large group of lactose-fermenters, many closely resembling *B. coli* as regards the methyl-red and Voges-Proskauer tests, but showing other different cultural characters. Most cultures of lactose-fermenters from fresh human faeces which would generally be classified as *B. coli* are unable to ferment cellobiose or utilise Koser's citrate medium for growth, but invariably produce indole from a suitable medium, and are able to ferment the dextrose of Eijkman broth at 46° C., with generation of gas. On the basis of these tests, only 11·2 per cent. of 223 cultures of lactose-fermenters from oyster and water samples from four districts were found to be *B. coli*.

Possibly no single differential test will be found entirely satisfactory for the identification of *B. coli*, and the following routine bacterial examination of water and oyster shell liquor is suggested. The liquid is cultured in Eijkman broth at 46° C., records of gas formation and plate-cultures of any tubes showing gas being made after 18 hours' incubation. The original tube cultures are replaced in the incubator at 46° C., and plate-cultures are again made from any tubes showing gas formation within 48 hours. Such plates, preferably eosin and methylene-blue, are incubated for 18–24 hours at 37° C., when one or more colonies of each different type of lactose-fermenter are transferred to (*a*) cellobiose, (*b*) citrate, (*c*) indole, and (*d*) lactose media, and kept at 37° C. for 24 hours. Only cultures giving negative cellobiose and citrate tests, producing indole, and fermenting lactose should be reported as *B. coli*. Until cellobiose becomes cheaper, the remaining three tests alone may be used with little risk of error. T. H. P.

Toxicological and Forensic.

Radium Poisoning. F. B. Flinn and S. M. Seidlin. (*Lancet*, 1929, Nov. 23, 1105–1106.)—Workers engaged in the manufacture or use of luminous paints are exposed to the dangers of radium poisoning, especially those workers who use the paints, since they point the camel-hair brushes with their lips. The radio-active substances are stored in the bones of the victims, chiefly in the cortex. This explains the bone changes and the fatal aplasia of the marrow, for 95 per cent.

of the rays coming from the bone are alpha rays, which are 10,000 times more destructive of human tissues than gamma rays. Removal from exposure, hygiene of the mouth, prevention and treatment of sepsis, and treatment of the anaemia which develops, have all been carried out in cases where symptoms have started. In addition, elimination of the dangerous substances from the bone has been attempted. Hunter and Aub, in 1927, used injections of parathormone (Collip's parathyroid extract) for the elimination of lead. This principle applied by Flinn and Seidlin (Parathormone in the treatment of Radium Poisoning, *Bull. Johns Hopkins Hosp.*, 1929, Nov., 269) to three girls with radium poisoning has caused gain in weight, improvement of the general condition, and great increase of the elimination of radio-active substance in the stools and expired air. P. H. P.

Medico-Legal Significance of Blood Groups. F. Schiff. (*Lancet*, 1929, Nov. 2, 921–922.)—The establishment of paternity by application of the rules governing the inheritance of the blood groups is now receiving a great deal of attention. The results obtained with this method were recently reviewed in a leading article in *The Lancet* (1928, **2**, 711), and some observations on this article are now made. The "blood test," far from being a method for the diagnosis of paternity, is, in certain cases, capable of merely excluding an alleged paternity. The method should, therefore, correctly be called "a test for the exclusion of paternity," but the exclusion of a man who has been denounced unjustly can be established in 1 out of 6 or 7 cases only, owing to the small number of blood groups existing. Exact data showing the extent and scope of the blood test have become available in Germany through an inquiry made by the author on behalf of a committee formed by the Reichsgesundheitsamt (see *Medizinische Welt*, August 24th, 1929). More than 5000 medico-legal examinations of this kind have already been made. Out of a total of 5500 law-suits (including some cases from outside Germany), the exclusion of paternity was decided upon in 8 per cent. of the cases. Taking into account that, theoretically, not more than 16 to 18 per cent. can be obtained, provided that in no instance an actual father is among those examined, then it may be stated that in those law-suits in which the blood test has been applied, roughly, every second man has been denounced unjustly. The application in the German Courts is given. Bernstein's formula of inheritance is generally accepted as the principle underlying the method; according to this formula, the rules governing the inheritance of blood groups, as discovered by von Dungern and Hirtzfeld, may be amplified in so far as the fatherhood of a man with the group AB in relation to a child O can be excluded, as well as the fatherhood of a man O in relation to a child AB. Amongst 5242 couples of mother and child, examined most carefully, in no instance was a combination found deviating from Bernstein's rule. It may safely be assumed that what is valid in relation to mother and child is equally valid in relation to father and child. In view of the importance already gained by this method the endeavour is made to ensure officially the reliability of the examination. Only a few especially competent experts shall be entitled to perform the examination. In Berlin, Frankfurt and Nürnberg there are special medico-legal experts

sworn in for making examinations of blood groups only. In some States (Bavaria, Saxony, Würtenberg) the examinations have been centralised in one or, at most, in a few institutes—*e.g.* university institutes of forensic medicine. As far as the serological technique is concerned, the principle has been accepted years ago that the diagnosis should be made on the ground of a cross-examination—*i.e.* the examination of the red cells and of the blood-serum each separately. In babies in which the formation of agglutinins is not yet accomplished, the test is repeated some months later. Examinations are made in several parallel series with various samples of test sera and test erythrocytes, respectively. In addition to the human serum of group B, used for diagnosis of the antigenic factor A, sera from rabbits immunised with sheep red cells have also proved valuable owing to their high titre and resistance. It is intended to submit all commercial test sera to Government control. (*Cf.* Martley, ANALYST, 1928, **53**, 14; and "Legal Notes," *id.*, 38.) P. H. P.

Agricultural.

Composition of Commercial Acid Lead Arsenate and its Relation to Arsenical Injury. H. S. Swingle. (*J. Agric. Res.*, 1929, **39**, 393–401.)—Commercial acid lead arsenates were found to contain 28·0 to 32·8 per cent. of arsenic, expressed as pentoxide (theoretical 33·1 per cent.), 0·16 to 1·40 per cent. of arsenious oxide, and 0·04 to 5·93 per cent. of water-soluble oxide (as As_2O_5). Experiments on Georgian peach trees showed that for concentrations below 0·01 per cent., and when present as soluble arsenic in acid lead arsenate, arsenious and arsenic acids are equally toxic, whilst at higher concentrations the latter has the greater toxicity. Arsenic is a cumulative poison, and the minimum amount toxic to peach leaves is equivalent to 0·0012 per cent. of the pentoxide. Soluble arsenic may be due to hydrolysis, which is accelerated by OH ions, or to the presence of incompletely oxidised arsenious oxide. It can be reduced to a minimum of 0·25 per cent. in acid lead arsenate without affecting the toxicity to insects, but even then the arsenate cannot be used safely in the absence of some material to prevent "burning" by the soluble arsenic. J. G.

Further Observations on the Occurrence of Protocatechuic Acid in Pigmented Onion Scales and its Relation to Disease Resistance in the Onion. K. P. Link, A. D. Dickson and J. C. Walker. (*J. Biol. Chem.*, 1929, **84**, 719–725.)—Link, Angell and Walker (*J. Biol. Chem.*, 1929, **81**, 369; ANALYST, 1929, **54**, 240) reported the isolation of protocatechuic acid (3, 4-dihydroxybenzoic acid) from the outer bulb scales of pigmented onions, and stated that the occurrence of this acid in the outer scales has a significant relationship to disease resistance in the onion. A more refined and accurate procedure for the extraction and isolation of the protocatechuic acid from pigmented onion scales is now given. With this procedure, which differs decidedly from the original, the authors have been able not only to obtain larger yields of the acid, but also to obtain the acid from bleached pigmented scales from which originally it could not be isolated. They find that

the quantity of protocatechuic acid in mature pigmented onion scales varies considerably and is correlated closely with the status of preservation of the pigments in the scales, being highest in those scales in which the pigment preservation is at a maximum. The unpigmented portions of the coloured onion scales (those regions near the top and neck of the bulb) either have only a small quantity of the acid or the acid is not present. Pigmented scales that have been badly leached by the action of meteoric or soil water, although some pigment may still be intact, contain little or no protocatechuic acid; protocatechuic acid has a relatively high solubility in water (1 to 55 parts at 14° C.), much greater than the solubility of the pigments with which it is associated in the coloured scales, and therefore the leaching action would be expected to reduce the concentration of the acid. The toxicity control experiments indicate that the maximum yield of protocatechuic acid so far obtained (0·125 grm. of acid per 100 grms. of fresh unbleached *red* scales, and 0·135 grm. of acid per 100 grms. of fresh unbleached *yellow* scales) accounts approximately for 35 to 40 per cent. of the toxicity of the extracts from which the acid was isolated. All the results so far obtained on the occurrence of protocatechuic acid in the outer scales of the pigmented onion (the so-called resistant types), is correlated with the field observations made with reference to the occurrence and development of the smudge disease. P. H. P.

Organic Analysis.

Detection and Determination of the Carboxyl Group by Distillation with Zinc Dust in a Stream of Hydrogen. A. W. van der Haar. (*Rec. Trav. Chim. Pays Bas*, 1929, **48**, 1170–1174.)—By distillation with zinc dust in a current of hydrogen from a retort on a sand-bath, as a general rule only those compounds which contain two oxygen atoms combined with a single carbon atom yield carbon dioxide. The only exceptions as yet observed are mannitol, quercitol, and phloroglucinol, which also yield the dioxide. Qualitatively, this method, furnishes an excellent means of distinguishing: (1) between carboxylic acids lactones and anhydrides on the one hand, and phenols on the other, and (2) with substances of high molecular weight, such as sapogenins, between carboxylic acids and phenols, the carboxyl group being otherwise difficult to detect in such cases. Quantitatively, however, the method is less accurate, although in many instances it serves to determine the number of carboxyl groups. Sulphur compounds may have a disturbing effect, since the baryta used for absorption of the carbon dioxide is rendered turbid with barium sulphite when compounds with two oxygen atoms united to one sulphur atom, like sulphonal and saccharin, are tested.

The procedure is as follows: The hydrogen, generated in a Kipp's apparatus from zinc and hydrochloric acid, is passed successively through a wash-bottle containing water and a soda-lime calcium chloride tower into a small long-necked retort connected with a suction flask, this in turn being connected with a wash-bottle containing baryta solution. The sand-bath may be a small sheet-iron box cut away to allow the neck of the retort to pass through the wall. The base of the

retort should be a few cm. from the bottom of the sand-bath. The retort is charged with about 10 grms. of pure zinc dust, and hydrogen is passed in a moderate stream through the apparatus until the air is displaced, and, with not too small a flame under the sand-bath, baryta solution is no longer rendered turbid. After cooling to some extent, the zinc dust is removed from the retort, mixed with 0·25 or 0·5 grm. of the substance, and returned. Hydrogen is then passed until the air is displaced, and the sand-bath heated, the gas current being continued until no further turbidity of the baryta solution is produced. The baryta flask is then removed, the precipitate being allowed to settle and washed by decantation with water free from carbon dioxide until the water no longer reacts alkaline. The precipitate is then filtered off and tested in the ordinary way for barium and carbonic acid. For quantitative purposes, the baryta flask is replaced by one or two Dennstedt's soda-lime apparatus, a wash-bottle with sulphuric acid and a calcium chloride tube being also inserted. The soda-lime apparatus is filled with hydrogen and weighed before the test, and at intervals of 30 or 60 minutes, until its weight remains practically constant. In general, the weight of carbon dioxide found is somewhat lower than the theoretical value. T. H. P.

New Method for the Determination of Neutral Fat in Sulphonated Oils. R. Hart. (*J. Amer. Leather Chem. Assoc.*, 1929, **24**, 576.)—It is suggested that neutral fats in sulphonated oils should be determined by saponification tests in which the "neutral fat saponification number" is determined, *i.e.* mgrms. KOH per grm. of total fatty matter. (Fatty matter is defined as animal or vegetable fats which react with alkali.) In addition to the present official methods for the analysis of sulphonated oils, the following saponification test is included:—*Saponification value of total fatty matter* (F°): From 2 to 2·5 grms. of the oil are boiled under a reflux condenser for 30 minutes with 25 c.c. of $N/2$ alcoholic potash. Fifty c.c. of alcohol are then added, and the solution boiled till all the ammonia is given off. The excess of alkali remaining is titrated with $N/2$ hydrochloric acid, phenolphthalein being used as an indicator. The amount of alkali absorbed by the fat is calculated to mgrms. KOH per grm. = F°. The free and combined fatty acids (B) (*ibid.*, 1927, 588), the alkali minus ammonia or fixed alkali (C) (*ibid.*) are determined in the usual way. From the above data the following formulae are derived:—

1. Saponification value of total fatty matter, plus fixed alkali of sample, mgrms. of KOH per grm. = F° + C.

2. Saponification value of total fatty matter, mgrms. KOH per grm.

$$V° = \frac{100(F° + C)}{\text{per cent. total fatty matter}}.$$

3. Saponification value of neutral fat, mgrms. KOH per grm.;

$$F_N = (F° + C - B).$$

4. Neutral fat, approximate per cent. of sample; $p = \frac{100\ F_N}{V^\circ}$.

5. Approximate saponification value of neutral fat, mgrms. of KOH per grm.;

$$V_N = \left(V^\circ - 10 + \frac{p}{10}\right).$$

6. Neutral fat, corrected, per cent. of sample; $P = \frac{100\ F_N}{V_N}$.

7. Neutral fat, corrected, per cent. of total fatty matter

$$= \frac{100\ P}{\text{per cent. total fatty matter}}$$

8. Saponification value of neutral fat, mgrms. KOH per grm.

$$= \frac{100\ F_N}{\text{per cent. total fatty matter}}$$

From the following table it will be seen that the saponification method gives results which are considerably higher than those obtained by extraction either with ether or petroleum spirit:

Method.	1.	2.	3.	4.
Petroleum spirit ..	—	—	5·02	8·78
Ethyl ether	12·05	16·64	9·14	15·06
By saponification ..	27·2	25·8	21·4	32·0

It would seem, therefore, that extraction of the original undecomposed oil by solvents does not yield all the neutral fat or all the fat that will react with alkali, and that some of the neutral fat is sulphonated, *i.e.* soluble in water and, therefore, incompletely extracted by solvents. R. F. I.

Colorimetric Determination of Turpentine in Air. P. Andrejew and A. Gavrilow. (*Chem. Ztg.*, 1929, **53**, 870–871, 889–891.)—The air is bubbled through a U-tube with a wide arm containing concentrated sulphuric acid at the rate of about 1·5 litres per minute, the acid run off from a tap at the bottom of the bend of the tube, and the apparatus washed with a further quantity of strong acid till 100 c.c. are obtained. The colour of an aliquot portion is matched in a Duboscq or other colorimeter against that of a suitable quantity of standard prepared by the addition of 1 drop of turpentine to 50 c.c. of concentrated acid weighed in a 100 c.c. flask. The flask and contents are re-weighed, well shaken for some time, and acid added to make 100 c.c. The colour produced varies from weak yellow for 0·1 mgrm. per 100 c.c. to orange-red for 100 mgrms. per 100 c.c., and should be matched within an hour. Extensive tests of the method showed that for colours produced by 2·5 to 100 mgrms. of turpentine per 100 c.c. of acid the accuracy (compared with the combustion method) is $\pm$ 0·02 mgrm. per litre of air, and that the presence of benzene or benzole (18 to 40 per cent.) has no marked

influence. The b.pt. of the standard (Russian) turpentine was 150° to 160° C., sp. gr., 0·8650, $n_D^{17·5}$ 1·4702 and α_D^{15} 25·78°. A solution of 200 mgrms. of diamine yellow and 2·8 mgrms. of methyl orange in a litre of water gives a colour standard stable for a week, 7 c.c. of which diluted to 100 c.c. matches 2·14 mgrms. of turpentine per 100 c.c. of acid. J. G.

Detection of Linseed Oil in Soya Bean Oil. J. F. Carrière. (*Chem. Weekblad*, 1929, **47**, 575.)—For pure soya bean oil the quotient $(I-126·19)/H$ is greater than 11, where I is the iodine value and H the insoluble bromide value as a percentage (*vide infra*). It may be considerably higher for a fresh oil, since, though I remains constant, H may fall off (*e.g.* from 0·55 to 0·20) in the course of a year. As a result of analyses of expressed soya bean oils, a somewhat higher figure (12) for the border-line value of the quotient was obtained on account of the lower values of H. If H' is the insoluble bromide value of the soya bean oil in a mixture containing X per cent. of linseed oil, then $X=100\ (H-H')/(y-H')$, where y may vary from 32·5 to 44. H is determined on 2 grms. of neutral oil (previously shaken with 10 per cent. sodium hydroxide solution and filtered), dissolved in 40 c.c. of ether in the presence of 5 c.c. of glacial acetic acid. Bromine (0·8 c.c.) is added in drops from a burette, and, after 3 hours at 0° C., the precipitate is filtered off in a tared glass crucible, washed with four 10 c.c. portions of ether at 0° C., and dried at 100° C. till constant in weight. J. G.

Determination of Citronellal. H. I. Waterman and E. B. Elsbach. (*Rec. Trav. Chim. Pays Bas*, 1929, **48**, 1087–1091.)—It has been suggested that the hydrochloric acid formed in determining citronellal by means of alcoholic hydroxylamine hydrochloride solution may lead to erroneous results. The experiments now described show that this is actually the case, since, in presence of 0·1 *N* alcoholic hydrochloric acid at 0° C., citronellal readily undergoes change. This destruction of part of the citronellal before it has reacted with the hydroxylamine may be avoided by the use of either hydroxylamine acetate or free hydroxylamine. The method is, however, subject to interference from the presence of peroxides, high results being obtained; similarly, Ferguson and Parry (*Schimmel Ber.*, 1929, 153) found that with oxidised oils high citral contents are indicated. There is a possibility that, in the action of "citronellal peroxide" on hydroxylamine, the citronellal may be regenerated, and thus be rendered capable of fixing free hydroxylamine. Experiment shows, indeed, that the products of oxidation of citronellal, freed from unchanged citronellal by distillation in a cathode light vacuum, yield apparent citronellal contents when analysed by the usual hydroxylamine hydrochloride method. This is also the case with the original citronella oils, although in these products the oxidation phenomena are kept more in the background by the presence of protective substances. T. H. P.

Detection and Determination of Chestnut Wood Extract in a Mixture of other Tanning Extracts. Committee Report. F. F. Marshall. (*J. Amer. Leather Chem. Assoc.*, 1929, **24**, 567.)—A method is described whereby

catechol tans and pyrogallol tans may be differentiated in unmixed solution. Fifty c.c. of the analytical solution of the tanning material are allowed to stand in a separating funnel with 5 c.c. of a 50 per cent. solution of iodic acid. The iodine liberated is all extracted by shaking with 2 or 3 portions of carbon tetrachloride, the mixed extracts being washed free from iodic acid with water. Twenty c.c. of 50 per cent. potassium iodide are added, and the iodine titrated, with repeated shakings, with $N/50$ sodium thiosulphate solution in the presence of starch. The results obtained expressed as grms. of iodine liberated per 100 grms. of tannins, were as follows:—*Catechols*: mimosa, 0·31; hemlock, 0·31; gambier, 0·31; logwood extract, 0·63; mangrove extract, 0·31. *Pyrogallols*: chestnut extract, 21·79; valonea, 21·50; myrobalans, 21·06; European chestnut extract, 18·77. Some other values obtained were: Oak bark, 3·47; gallic acid, 21·79; pyrogallic acid, 43·58; and pyrotechu, 39·34. From these figures it is concluded that the common tanning materials are catechuic and gallic rather than a mixture of pyrogallic and gallic. It is claimed that it is possible to determine the tannin in pure extracts of pyrogallol tannins by this method by calculating to tannic acid, assuming 322·15 as its atomic weight, and that iodic acid oxidises two parts of tannic acid. The table shows the comparison between this method and the official method, expressed as percentage of tan.

	Official method.	Iodic method.
Chestnut	27·43	28·14
Chestnut	29·46	30·02
Myrobalans	31·29	32·47

A method is given whereby oak and chestnut can be separated from all other tanning materials. To one part of non-tan, add one part of $N/10$ potassium dichromate solution and 0·5 c.c. of $N/10$ sulphuric acid, and heat to boiling. Under these conditions oak and chestnut give a heavy precipitate. The oak and chestnut may then be separately recognised by the addition of ammonia to the non-tans, when the presence of oak is shown by the formation of a blue colour.

R. F. I.

Inorganic Analysis

Sampling and Analysis of Alloys. O. Bauer and E. Deiss. (*Z. anal. Chem.*, 1929, **79**, 47–53.)—The difficulties encountered in obtaining representative samples by the usual method (*e.g.* drilling) are exemplified by analyses made of different parts of an ingot of gun-metal, the observed variations being: Copper 81·98 to 83·67, tin 4·66 to 5·85, and lead 2·74 to 3·48 per cent.; the zinc content (about 7·8 per cent.) was fairly constant throughout the ingot. The variations are due to segregation or de-mixing during solidification. The most representative sample is obtained when the ingot is cut across at right angles to its longitudinal axis, and the whole surface of the cross-section planed or filed. Even this method does not take into account the greater segregation at the two extremities of the ingot, but this error is reduced in proportion of the increasing length of the ingot

as referred to its cross-section. It is further recommended to take the whole of the particles obtained in one filing or planing for the determination of each constituent. W. R. S.

Precipitation of Copper by Thiosulphate. J. Majdel. (*Z. anal. Chem.*, 1929, **79**, 38–44.)—The method was submitted to a critical examination, and the results found to compare within 0·05 per cent. with those obtained by electrolysis, when the following conditions are observed: Hydrochloric or nitric acid is removed by evaporation to dryness or, if sulphuric acid is also present, to the fuming stage. After solution in water, the acidity is adjusted to 25 c.c. of strong sulphuric acid in a total bulk of 150 c.c. A boiling solution of sodium thiosulphate (5 grms.) in water (50 c.c.) is added all at once to the boiling copper solution (maximum, 0·4 grm. CuO), which is stirred during the addition. After short boiling (½ to 2 minutes), the precipitate is collected, washed with boiling water, dried, and ignited with the filter over a blast burner; it is then cooled, crushed with a glass rod, and again heated at a temperature exceeding 900° C. The precipitate is weighed as CuO. Cadmium is not precipitated; other members of the hydrogen sulphide group interfere. Hydrochloric and nitric acids should be removed as described above. W. R. S.

New Reagent for Cadmium. Evrard. (*Ann. Chim. anal.*, 1929, **11**, 322–326.)—The reagent is prepared by the combination of molecular proportions of allyl iodide and hexamethylenetetramine in chloroform solution. The base forms colourless crystals very soluble in water, all of the iodine being in ionic solution. Cadmium solutions give with the reagent a crystalline precipitate, of characteristic appearance under the microscope. The composition is represented by $CdI_2.2[(CH_2)_6N_4.C_3H_5I]$, with 11·44 per cent. of cadmium. For its quantitative determination, 10 c.c. of the sulphate solution are poured into 30 c.c. of a cold solution of the reagent (strength not given). The precipitate is collected in a porous glass crucible, washed with a solution of the precipitant, then with 96 per cent. alcohol, dried, and weighed. Zinc is not precipitated; the reaction is not affected by sulphuric acid of 0·5 *N* concentration. W. R. S.

Rapid Gravimetric Determination of Cadmium as Oxalate. J. Dick. (*Z. anal. Chem.*, 1929, **78**, 414–417.)—The cold, neutral nitrate or sulphate (not chloride) solution (50 to 100 c.c.) is treated with a moderate excess of ammonium oxalate solution, followed by one-third the total volume of 95 per cent. alcohol. After 15 minutes' standing, the crystalline precipitate is collected in a porous crucible, washed 6 to 8 times with 50, then with 95, per cent. alcohol, lastly with ether. Suction is continued for a few minutes after completed washing, or the drying is done *in vacuo*. Factor for Cd: $CdC_2O_4.3H_2O$: 0·4418. The method is not applicable in the presence of alkali or ammonium salts. W. R. S.

Analysis of Sodium Bismuthate by a Gasometric Method. T. Somiya and K. Kawai. (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 249B.)—In the presence of cobalt nitrate, sodium bismuthate is decomposed by sulphuric acid, with liberation

of oxygen, which reaction the authors find to be quantitative. The apparatus used (Treadwell and Hall, *Analytical Chemistry*, p. 340) comprises a 100 c.c. gas burette and a decomposition bottle in which 1 grm. of the sample is placed, together with 30 c.c. of 4 *N* sulphuric acid and 0·1 to 0·3 c.c. of a saturated solution of cobalt nitrate. The decomposition bottle is kept in hot water for 5 to 15 minutes, with occasional shaking, the volume of the evolved gas being measured at room temperature after removal of the carbon dioxide by potash bulbs. The percentage of sodium bismuthate is computed from the volume of the gas corrected to N.T.P. In three experiments, 68·4, 67·8 and 67·8 per cent. of sodium bismuthate were obtained, whereas, by the permanganate method, the result was 68·2 per cent.

R. F. I.

Volumetric Determination of Cobalt in Potassium Cobaltinitrite. A. A. Wassilieff. (*Z. anal. Chem.*, 1929, **78**, 439–442.)—The solutions containing 0·02 grm. of Co, were evaporated to about 10 c.c., and treated with 8 c.c. of 50 per cent. potassium nitrite solution, then with 5 to 8 drops of glacial acetic acid. After 12 to 18 hours, the precipitate is collected in a porous glass crucible; the dish is rinsed with portions of the mother-liquor, and the washing effected with saturated potassium sulphate solution. The crucible containing the precipitate is introduced into a conical 600 c.c. flask and treated with 250 c.c. of water, 50 of 0·1 *N* permanganate, and 35 of sulphuric acid (1:1) in the order given. The liquid is warmed to 50° C. and stirred from time to time till the precipitate is decomposed. After complete cooling, 2 to 3 grms. of potassium iodide are added, and the flask stoppered and gently shaken until complete solution of the higher manganese oxide has taken place. The liberated iodine, being the measure of the excess permanganate used, is titrated with 0·1 *N* thiosulphate. One c.c. of 0·1 *N* permanganate = 0·0005361 grm. Co.

W. R. S.

Detection of Traces of Potassium in Presence of Zirconium. R. D. Reed and J. R. Withrow. (*J. Amer. Chem. Soc.*, 1929, **51**, 3238–3241.)—Phosphoric acid or phosphates, introduced for the removal of the zirconium, interfere with the subsequent detection of potassium by sodium cobaltinitrite. Precipitation of the zirconia by ammonia and removal of the ammonium salts by volatilisation, permit of the use of the cobaltinitrite test. A rapid method for the detection of potassium consists in converting the zirconium salt into a complex by addition of tartaric acid, neutralising with sodium hydroxide, and acidifying slightly with acetic acid; the cobaltinitrite reaction can then be carried out.

W. R. S.

Determination of Traces of Iron by Photochemical and Colorimetric Methods. B. S. Sharma. (*J. Soc. Chem. Ind.*, 1929, **48**, 336T.)—Traces of ferric or ferrous iron may be colorimetrically determined by noting the intensity of the pink colour produced in sunlight when the iron solution is added to a saturated solution of ammonium thiocyanate; this is proportional to the amount of iron present. The comparison is made with the original solution, which has been kept in the dark. The iron may also be determined photochemically, since the time of

disappearance of the pink colour in the dark is also proportional to the amount of iron present, and $Q/T=K$ for Q in grms. and T in minutes, and $K=0{\cdot}118\times10^{-11}$. If ordinary ammonium thiocyanate is used, a control is necessary, owing to the presence of traces of iron. Strong diffused daylight, or light from an iron arc or mercury vapour lamp, may be used, and precautions against contamination by iron from glass vessels, filter papers, etc., are necessary. Factors affecting the disappearance of the colour are: concentration of the ammonium thiocyanate solution, amount of free acid present and temperature, and further work on these points is being carried out. The time of disappearance of colour in the dark after 10 minutes' exposure to the sun was from 15 minutes for $1{\cdot}7762\times10^{-11}$ iron, to 150 minutes for 10 times the quantity. D. G. H.

Reviews.

CATALYTIC PROCESSES IN APPLIED CHEMISTRY. By T. P. HILDITCH, D.Sc., F.I.C. Vol. II of a Series of Monographs on Applied Chemistry, edited by E. Howard Tripp, Ph.D. Pp. xx+360. London: Chapman & Hall, Ltd. 1929. Price 16s.

The editor, in his preface, in discoursing upon the duties of a writer of monographs such as this, says, "he must pick out the plums to save others from the indigestion that follows the eating of the whole pie." Now that is exactly what Professor Hilditch has done, for the book is full of plums; nevertheless, the author has not fallen to the temptation of elaborating the more spectacular achievements of industrial catalytic processes; on the contrary, the reader cannot fail to be struck by the systematic manner in which the whole subject has been treated.

Of all the processes which are applied in modern chemical industry, there is certainly none that affects a greater number of different industries than do those whose operations are dependent on catalytic action. Consequently a subject of such wide application, offering, as it does, scope for the production of many volumes, is all the more difficult to compress into a moderate-sized book, maintaining at the same time a happy balance between the desire to say too much on one process and too little on another.

Some idea of the scope may be realised by a mere glance at the Table of Contents, which is followed by two classified lists in which over 50 processes and 100 products are tabulated. These lists alone provide food for much study, apart from their utility for easy reference to the subject matter. They are so instructive that the book is worth purchasing for these tables alone. So complete indeed are they that it was an almost impossible task to find any process left out that should be included; in fact, the hydrogenation of pyridine to piperidine, and indigo to indigo white seem to be the only omissions. The former is dealt with in various publications; for example, by Skita, *Rept. German Chem. Soc.*, 1916, **49**, 1597; and Zelinsky, *ibid.*, 1924, **57**, 150. These names, incidentally, do not appear in

the very useful index of names preceding the index of subjects at the end of the book, but, in spite of this, the author is to be complimented on the very excellent bibliography to be found at the end of each chapter.

The book is divided into four sections, which may be briefly described under the headings of:—I, General Principles; II, Heterogeneous Catalysis; III, Fermentation Processes; and IV, Homogeneous Catalysis. Of these, the practical utility of the Section on Fermentation in this volume may be questioned, but its inclusion is theoretically defensible, and no one who reads it would ever wish for its deletion.

The hydrogenation of fats is adequately dealt with in some 21 pages, in which not only are the basic principles of the different systems contrasted, from the oldest to the latest, but the various methods of hydrogen production and purification, their merits and defects, are described; and this without overlapping the catalytic production of hydrogen dealt with in an earlier chapter.

It would be quite impossible in a short review to go into any particulars of the processes dealt with, which include such important ones as sulphuric acid, synthetic ammonia, and alcohol manufacture.

Types of catalyst and their action are very fully discussed from both practical and theoretical standpoints.

The reader of this review might ask wherein lies the use of this work to the analyst, and it must be admitted that there is little, if anything, which deals with analytical chemistry directly; but the modern analyst cannot confine himself to the mere determination of constituents; he must understand the industrial processes by which the products he tests are produced.

No one can be an analyst who is not first a chemist, and no chemist should allow himself to be ignorant of the processes dealt with in this volume, which are presented in a manner so easy of reference, and so clear in description. Moreover, it is often surprising how a process, which has been elaborated with the sole object of manufacture, provides a reaction which can be used in the laboratory as an analytical test.

While one would like to have seen the inclusion of illustrations, one cannot help feeling that their introduction would have expanded the book beyond convenient size.

E. R. BOLTON.

ENZYME ACTIONS AND PROPERTIES. By ERNST WALDSCHMIDT-LEITZ. Translated and extended (from the German) by ROBERT P. WALTON. Pp. xv+255. New York: John Wiley & Sons; London: Chapman & Hall. 1929. Price 20s.

The object of this book is to give a concise presentation of the principles of enzyme action. Written originally by a former colleague of Prof. Willstätter, the text is concerned largely with the work emanating from the school of that great chemist. Although dealing principally with recent researchs on the subject, the fundamental observations of Liebig, Pasteur, Mitscherlich, Berzelius,

Berthelot, Traube, Hoppe-Seyler, and others are cited, yet there is no reference to some of the work of the latter portion of the nineteenth century.

A concise manual of this kind should appeal to the analytical chemist, in view of the increasing use of methods in which enzymes are likely to find application as reagents in both qualitative and quantitative analysis. Thus for methods involving hydrolysis, enzymes, unlike the general hydrolytic agents—acids and alkalis—are in most cases specific, and when better methods have been devised for their purification, we may hope that preparations possessing absolute specificity may be available.

The book comprises a "General Section" (100 pp.) of seven chapters, and a "Special Section" (141 pp.) of eight chapters, together with the author and subject indexes. References are given in footnotes to the more important original papers.

Enzymes are defined as *definite material catalysers of organic nature with specific powers of reaction, formed indeed by living cells, but independent of the presence of the latter in their operation.* The hypothesis of Ostwald, that the action of enzymes as catalysers consists only in the acceleration of reactions already in progress without themselves being altered by the reaction, is accepted. With regard to the material nature of enzymes, however, it is admitted that no success has been attained as yet by the Willstätter school in positively identifying any known enzyme as a chemical entity. It appears to have been established that the activity of these agents is always exhibited in the colloidal state.

The idea that the effectiveness of enzymes depends on their electric charge, and that they exhibit the phenomenon of kataphoresis, was first put forward by Loeb in 1909, and later, developed by Michaelis, who regards them as amphoteric electrolytes. The researches carried out in the Willstätter school indicate, however, that in some enzymes basic, and in others acidic, properties predominate. Further, when a certain degree of purification has been attained by adsorption and elution, an enzyme may change its sign. Thus, sucrase of yeast is only adsorbed by electro-negative kaolin when it has been purified up to a certain degree, whilst pancreatic amylase is only adsorbed by electro-positive alumina gels when in the crude state. All these points are dealt with in the book, and the view held by Emil Fischer and by H. E. and E. F. Armstrong, that combination of enzyme and substrate precedes catalytic changes, is accepted. The quantitative determination of enzymes, depending on the increased velocity of the reactions which they promote, based on the law of mass action, is dealt with in a special chapter, and also in other parts of the book under specific enzymes.

We may point out that the translator should have altered certain symbols from the original German. Thus "sucrase unit" should be (S.U.), and not (S.E.); "sucrase value" should be (S.V.), and not (S.W.). Other similar cases could be cited. Referring to the distinction, formerly adopted, of "organised" and "unorganised" ferments, the translator uses the terms "formed" and "unformed" ferments. Again, "preparate" is used instead of "preparation."

A book written by so eminent an authority as Professor Waldschmidt-Leitz

cannot fail to be of value; but, taking a general survey, in our opinion, its sequence might be improved. We think also that the text is in some cases too diffuse, whilst in others the matters dealt with are not sufficiently explained, and need supplementing by reference to the original papers cited. The want of references is specially noticeable in regard to the kinetics of enzyme action. The book will be of service mainly to those already acquainted with the subject, whilst to others it will be found not sufficiently explicit, so that its object has not been completely attained. ARTHUR L. LING.

DIE ROLLE DER ZYKLISCHEN AMINOSAUREANHYDRIDE IN DER NEUEREN STRUKTURCHEMIE DER PROTEINE. Von Dr. EMIL KLARMANN, Chef-Chemiker der Lehn and Fink Incorporated in Bloomfield, New Jersey. Pp. vi+93. Berlin and Wien: Urban and Schwarzenberg. 1929. Price Mk. 9.

Zelinsky's discovery, a few years ago, that some proteins contain as much as 80 per cent. cyclic compounds, came as a shock to organic chemists, who had regarded Emil Fischer's polypeptide formula for the proteins as finally established. The present monograph has been written by Klarmann at the suggestion of Abderhalden who is carrying on the researches of Emil Fischer. It is an attempt, which at most can only be regarded as partially successful, to re-establish Fischer's polypeptide formula. The final decision must of necessity be left to the future; but to a present-day observer it seems as if Fischer's ideas will have to be replaced by other working hypotheses, and our views on the proteins revised. Should this be so, Fischer's classic researches, in common with many other great men's contributions to chemistry, will have to pay the penalty of progress.

Dr. Klarmann's monograph, none the less, forms most interesting reading, and his treatment of the subject is comprehensive. It will be welcomed by many who have felt the need of a clear and penetrating review of the conflicting ideas as regards the constitution of the proteins. M. NIERENSTEIN.

POLAR MOLECULES. By P. DEBYE, Ph.D. Pp. 172. New York: Chemical Catalog Co. 1929. Price $3.50.

This book deals with the subject of polar molecules from the standpoint of the mathematical physicist; and, though it contains many subjects of interest to the chemist, the treatment is so mathematically thorough that probably very few chemists will be able to take full advantage of it. Its appeal to the chemist, however, lies in the correlation of the dielectric behaviour of molecules with such physical properties as refraction, optical dispersion and absorption, which have been found to have a direct bearing on chemical structure. The possible structures of the hydrogen halides, water and ammonia, are discussed. Among the other subjects treated are: Anomalous dispersion produced with radio-frequencies, electrical saturation effects (dielectric constants of liquids in strong electric fields, dielectric constants of ionic solutions), dielectric phenomena and the quantum theory, energy levels and wave mechanics, rotating molecules.

The book is well produced, and, being an authoritative exposition of this

difficult subject, will be heartily welcomed by investigators in this particular field of scientific activity. HUBERT T. S. BRITTON.

PHOTO-PROCESSES IN GASEOUS AND LIQUID SYSTEMS. By R. O. GRIFFITH, D.Sc., and A. MCKEOWN, D.Sc. Pp. viii+691. London: Longmans, Green & Co. 1929. Price 25s. net.

In 1914, Sheppard's book on Photo-chemistry was published in this series of "Textbooks of Physical Chemistry." Since that time this branch of chemistry has made such progress that the authors have found it advisable to limit the contents of their book to a study of gaseous and liquid systems. Moreover, photochemistry has become so specialised that the present volume, like Baly's Spectroscopy, takes on the characteristics of a monograph rather than those of a textbook, such as was the first volume in this series.

In their preface the authors state that the foundations on which the present-day photo-chemist must build are those branches of modern physical theory which are concerned with the interaction of radiation and matter, and include the theory of atomic and molecular structure, atomic and molecular spectra, and photo-luminescence. They have, therefore, devoted nearly half the book to these topics. In addition, there is included a chapter on chemiluminescence—the inverse phenomenon to photochemical change—and its interpretation along modern physical lines. This portion of the book will be found hard reading for a chemist, unless he is well equipped mathematically and physically. A complete understanding of it is, however, not necessary as a preliminary to the study of the second part, which deals with photochemical reactions in particular. In this section the authors have had a very difficult task to co-ordinate the enormous mass of contradictory literature on the subject. How difficult it has been may be seen from their statements concerning the photochemical action between hydrogen and chlorine, of which they write (p. 521): "In spite of the valuable work carried out by both schools (Chapman at Oxford and Bodenstein in Berlin) during the past fifteen years, general agreement has not yet been reached in regard to certain of the experimental facts themselves, and, corresponding with this lack of agreement, widely different views regarding the mechanism of the photochemical process have been upheld." Again, on p. 543, "it is hardly an exaggeration to say that no two workers in this field hold the same views with regard to the theoretical interpretation of this reaction."

The difficult task has been accomplished in a very satisfactory and skilful manner. The treatment is as concise as one could expect under such conditions, and, what is more to the point, critical. Workers in the field of photochemistry should be grateful to the authors; they will find it necessary to have the book at their side ready for constant reference. T. SLATER PRICE.

CHEMICAL AFFINITY. By L. J. HUDLESTON. (Monographs on Inorganic and Physical Chemistry, edited by Alexander Findlay, D.Sc., F.I.C.). Pp. 138. London: Longmans, Green & Co., Ltd. Price, 7s. 6d. net.

This volume is one of the well-known series of monographs on Inorganic and

Physical Chemistry edited by Prof. Alexander Findlay, and, in the author's words, "seeks only to develop one aspect of the subject, namely, the use of thermal and equilibria data to assist in the design and control of new problems of reaction."

The author considers in turn the transformation of energy, entropy, free energy, solutions (and their activities), Nernst's heat theorem, and the third law of thermodynamics. The subject is treated from the point of view of the chemist of graduate standing, with fairly good mathematical equipment, who wishes to apply his knowledge of theoretical thermodynamics to practical problems. The last chapter, therefore, in which 20 applications of the theorems and equations deduced earlier in the book are discussed, is particularly valuable. Examples of special analytical interest are determinations of the stability of a mixture of finely powdered antimony trioxide and zinc prepared for the demonstration of the Marsh test, and of the degree of hydrolysis of silicon tetrafluoride by water vapour at high temperatures. Tables of data and references are also included.

The author is to be congratulated on his lucid treatment of a somewhat difficult subject, and on the fact that he has avoided difficulties of notation by adopting the system of G. N. Lewis, whose influence, indeed, is apparent throughout the book. A few obvious errors have been noted, and the rendering of the often mis-spelt name Kirchhoff is not that usually accepted; the word "constants" at the bottom of p. 121 should be replaced by "coulombs."

The work should serve a useful purpose by drawing attention to the fact that thermodynamical methods constitute a valuable weapon for the attack of numerous problems, including those of analysis, though their use is at present restricted, largely by lack of the necessary data. JULIUS GRANT.

ALLEN'S ORGANIC ANALYSIS, Vol. VII. VEGETABLE ALKALOIDS: PROPERTIES, REACTIONS, TOXICOLOGY, FOOD AND DRUGS CONTAINING ALKALOIDS. Fifth edition. Edited by C. AINSWORTH MITCHELL, D.Sc., F.I.C. Pp. xi+ 869. London: J. & A. Churchill. Price 30s. net.

Allen's Commercial Organic Analysis appears in every succeeding edition to become less like a manual of commercial analysis, but, it should be added, not less requisite to commercial analysts. The methods of analysis appear less conspicuous, but that is because the work contains ever more varied and abundant information on articles to be analysed.

Volume VII of the fifth edition deals with vegetable alkaloids, and also, as the cover states, with foods and drugs containing alkaloids. That alkaloids are contained in any foods may appear at first a strange suggestion, but pepper, which is technically a food, contains the alkaloid piperine, and there is now a general opinion agreeable to the inclusion of theobromine and caffeine among alkaloids, although these were formerly classified rigidly outside the group. Alkaloids also occur in the potato, particularly in the peel, in malt, and in the germ of barley. The bulk of the volume is, however, occupied with the more numerous and more interesting group of alkaloids derived from vegetable drugs, many of which find

application in medicine. These are described in separate monographs, each being the work of a writer chosen for his special knowledge of the subject or section.

There is an introductory article by Dr. Henry dealing with the distribution and mode of occurrence of alkaloids, their function in plants, nomenclature, methods by which they are isolated and estimated, and their properties. There follows a list of sixteen of the more important reagents which cause precipitation of the alkaloids, with accounts of their behaviour. A description of colour tests and other peculiar reactions completes an interesting and useful monograph.

The introduction is followed by a General Section, in which individual alkaloids other than those which are of special commercial importance in connection with food or drugs are dealt with systematically by Mr. T. M. Sharp.

There is an extensive treatise on coffee by Dr. J. J. Fox and Mr. Sageman, to which is appended a monograph on chicory. Kola and Guarana, which also contain caffeine, and are used for making beverages in the countries where they are indigenous, receive attention, and the constituents of maté, the tea of Paraguay, are also enumerated. There is a long monograph on tea by the same authors, containing much information on all the different varieties, green, black, hyson, and others—the only thing the reviewer missed was a statement describing what gunpowder-tea is. Cocoa and chocolate are efficiently dealt with by Mr. R. Whymper.

The treatment of the subject-matter follows in some cases the line of a general discussion on the vegetable materials from which the alkaloids are derived, and the discussion is extended to associated products which are non-alkaloidal. Thus, under pepper, descriptions are found of piperic acid and of the essential oil of pepper, followed by an article dealing with the adulteration of pepper. Whether this arrangement is better than the plan of grouping essential oil of pepper with essential oils, and piperic acid with kindred acids, it is not easy to say. Such questions can only be decided by the experience of those who use the book.

The arrangement of matter dealing with the great groups of alkaloids, such as those of Cinchona (by Mr. Chick), Opium (by Mr. F. O. Taylor), Nicotine and Tobacco (by Mr. R. W. Tonkins), Cocaine (by Mr. Norman Evers), etc., is instructive as well as easy for reference. The article revised by Dr. C. A. Mitchell is an excellent treatise on the Strychnos alkaloids. The description of the tropine bases (by Dr. F. Carr) presents a comparison of the relationships and differences of the whole group of mydriatic alkaloids.

The information given appears generally to include all that has ever been published relating to individual alkaloids, and references to authorities are quoted in every connection sufficient to enable the reader to consult original memoirs. But this must not be allowed to suggest that the work is only a compilation of published facts; that impression would be wrong. The text is discriminative, and generally gives a plain indication of the merits and defects of the analytical processes described. The volume has been very carefully prepared. It has been a laborious work to produce, and is one worthy of the name of its founder, as well as of those who have contributed to its reconstruction. THOMAS TICKLE.